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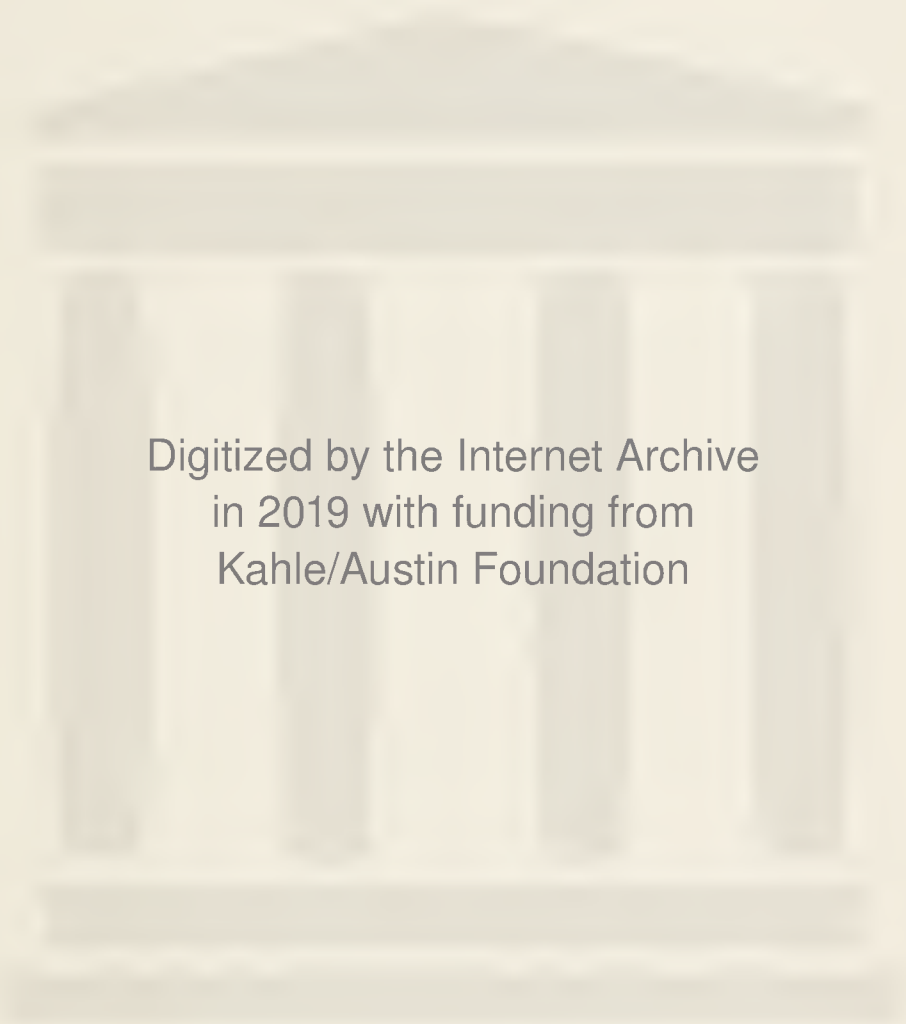

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ADVANCES IN CHEMICAL PHYSICS

VOLUME XIII

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ADVANCES IN CHEMICAL PHYSICS

Edited by I. PRIGOGINE
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VOLUME XIII

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INTRODUCTION

In the last decades, chemical physics has attracted an ever-increasing amount of interest. The variety of problems, such as those of chemical kinetics, molecular physics, molecular spectroscopy, transport processes, thermodynamics, the study of the state of matter, and the variety of experimental methods used, makes the great development of this field understandable. But the consequence of this breadth of subject matter has been the scattering of the relevant literature in a great number of publications.

Despite this variety and the implicit difficulty of exactly defining the topic of chemical physics, there are a certain number of basic problems that concern the properties of individual molecules and atoms as well as the behavior of statistical ensembles of molecules and atoms. This new series is devoted to this group of problems which are characteristic of modern chemical physics.

As a consequence of the enormous growth in the amount of information to be transmitted, the original papers, as published in the leading scientific journals, have of necessity been made as short as is compatible with a minimum of scientific clarity. They have, therefore, become increasingly difficult to follow for anyone who is not an expert in this specific field. In order to alleviate this situation, numerous publications have recently appeared which are devoted to review articles and which contain a more or less critical survey of the literature in a specific field.

An alternative way to improve the situation, however, is to ask an expert to write a comprehensive article in which he explains his view on a subject freely and without limitation of space. The emphasis in this case would be on the personal ideas of the author. This is the approach that has been attempted in this new series. We hope that as a consequence of this approach, the series may become especially stimulating for new research.

Finally, we hope that the style of this series will develop into something more personal and less academic than what has become the standard scientific style. Such a hope, however, is not likely to be completely realized until a certain degree of maturity

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has been attained—a process which normally requires a few years.

At present, we intend to publish one volume a year, but this schedule may be revised in the future.

In order to proceed to a more effective coverage of the different aspects of chemical physics, it has seemed appropriate to form an editorial board. I want to express to them my thanks for their cooperation.

I. PRIGOGINE

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FIRST PASSAGE TIME PROBLEMS IN CHEMICAL PHYSICS*

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I. INTRODUCTION

There are many processes in chemical physics that require the calculation of rates or rate constants. In several of these calculations one assumes that the underlying process can be described in terms of stochastic models, and more specifically in terms of the properties of random walks. Chandrasekhar[1] has given an excellent introduction to some of these topics. There is one class of problem, mentioned only briefly in his article, that has recently found increasing application in many fields of chemical physics, namely, first passage time problems. As an example, several authors[2–4] have proposed models for the dissociation of diatomic molecules in which dissociation occurs when the molecules acquire a certain critical energy E_C through collisions. If the changes in energy can be described in probabilistic terms, then the time to reach E_C is known as the first passage time. Since the theory of first passage times plays an integral role in the formulation of many models in chemical physics, and since no general account of the theory is to be found in chemical literature, various techniques useful for solving such problems are collected below.

In order to define a first passage time problem we consider a space Ω that can be decomposed into two non-overlapping sub-

* This paper was presented at the La Jolla Summer School on Chemical Physics, August 1965, University of California, San Diego, California, U.S.A.

spaces V and $\bar{V}$. It will be assumed that initially the random variable of interest lies in the subspace V: the first passage time is defined to be the time elapsing before passage to $\bar{V}$ for the first time. For example, in the dissociation model mentioned above Ω would consist of all energies, the space V would be all energies satisfying $E < E_C$, and $\bar{V}$ would consist of all energies satisfying $E \geq E_C$. In more elaborate dissociation models several quantum numbers might be involved, in which cases Ω would be multi-dimensional.

There are many specific models involving first passage times to be found in the literature. The first of these appears to have been developed in connection with Brownian motion studies by Schrödinger[5] and by Smoluchowski.[6] A first passage time model is relevant in the discussion of the Ehrenfest urn model,[7] in the theory of escape of stars from star clusters,[8] in the theory of reaction rates,[2–4] and in certain problems in the theory of poly-electrolytes.[9] Although there is a considerable mathematical literature on first passage time problems,[10] there have been few publications in the physical or chemical literature on the subject.

Although our principal concern in this article will be first passage problems for Markov processes it is well to point out that there are occasional applications which are non-Markovian in nature. As an example the recurrence of colloid counts in a fixed volume as in the experiments of Svedberg[11] and Westgren[12] analysed by Smoluchowski,[13] is a fundamentally non-Markovian process. Although Smoluchowski's early analysis did not make use of any assumption of Markovian evolution Chandrasekhar's later account[1] erred in deriving the fundamental relations. This error was pointed out by Bartlett, who gave a more complete account of the general problem.[14] Some related material is also to be found in a paper by Siegert.[15] Most applications, however, fall under the heading of Markov processes, which will be the subject of our future developments.

The plan of the present article is as follows: Section II contains a general account of the calculation of first passage time moments for Markov processes in continuous time, together with the specialization to the case of a discrete set of states. Section III contains the specialization to systems where the transition probabilities satisfy a Fokker–Planck equation.

II. GENERAL FORMULAE FOR MOMENTS OF THE FIRST PASSAGE TIME

We shall label the random variable of interest X(t), which can be a vector or a scalar. It will be assumed that the development of X(t) in time can be described as a stationary Markov process. To describe the statistical properties of X(t) we choose a probability density $p(x,t|y)$, defined so that $p(x,t|y)dx$ is the probability that $x < X(t) \leq x + dx$ given that $X(0) = y$, i.e., y is the initial position. When X(t) takes on integer values only $p(n,t|m)$ will be the probability that $X(t) = n$, given that $X(0) = m$. In both cases the variables x or n can refer to multidimensional vectors unless otherwise noted. The function $p(x,t|y)$ in general satisfies a linear operator equation of the form:

$$\partial p/\partial t = -L_x p, \tag{1}$$

where L_x operates on x only, and where $p(x,0|y) = \delta(x - y)$ for X continuous, and $p(x,0|y) = \delta_{xy}$ for X discrete. To encompass both cases we introduce the symbol $\Delta(x - y)$ which will denote a delta function or a Kronecker delta depending on whether x and y are continuous or discrete. When X is continuous the most commonly used form for L_x is the Fokker–Planck operator which in one dimension is

$$-L_x = \frac{1}{2} \cdot \frac{\partial}{\partial x}\left(a_2 \frac{\partial}{\partial x}\right) - \frac{\partial}{\partial x}(a_1), \tag{2}$$

where a_1 and a_2 are the first and second moments of the infinitesimal transition rates.[1] When X is discrete, as is the case for many quantum problems, L_x is a difference operator. There appears to have been no study of the case of mixed discrete and continuum problems, although they do arise in the context of neutron thermalization.

The probability that X(t) is still in V at time t given that it started at y in V will be denoted by $p_V(y,t)$ and is given by

$$p_V(y,t) = \int_V p(x,t|y)dx. \tag{3}$$

Let $\eta(y,t)$ be the probability density for the first passage time: that is, if T is the first time that X(t) reaches $\bar{V}$, given that

$X(0) = y$, then $\eta(y,t)dt$ is the probability that $t < T \leq t + dt$ given that $X(0) = y$. An expression for $\eta(y,t)$ is obtained by noting that if $X(t)$ is in V at time t, then it either makes a first passage in $(t,t + dt)$ or it remains in V at $t + dt$. These two possibilities lead to

$$p_V(y,t) = \eta(y,t)dt + p_V(y,t + dt) \tag{4}$$

or

$$\eta(y,t) = -\partial p_V(y,t)/dt. \tag{5}$$

Moments of the first passage time are defined by

$$\langle t^n(y)\rangle = \int_0^\infty t^n \eta(y,t)dt = n \int_0^\infty t^{n-1} p_V(y,t)dt, \tag{6}$$

$$n = 1, 2, \ldots$$

where the last form is obtained by an integration by parts.

We can obtain other, formal, expressions for the moments in terms of the operator L_x by starting from the formal solution to eq. (1):

$$p(x,t|y) = e^{-L_x t}\, \Delta(x - y). \tag{7}$$

Substituting this expression into eqs. (3) and (6) we find

$$\langle t^n(y)\rangle = n \int_0^\infty t^{n-1}dt \int_V e^{-L_x t}\, \Delta(x - y)dx \tag{8}$$

$$= n! \int_V L_x^{-n}\, \Delta(x - y)dx,$$

where we have freely interchanged orders of integration.

In order to use eq. (8) for computation we must introduce a more explicit representation of the quantities involved. When $X(t)$ ranges over the integers, the operator L_x can be represented as a matrix $\mathbf{L} = (L_{mn})$, Eq. (3) becomes

$$p(n,t|m) = (e^{-\mathbf{L}t})_{nr}\delta_{rm} = (e^{-\mathbf{L}t})_{nm}, \tag{9}$$

and the r'th moment of the first passage time conditional on $X(0) = m$ is

$$\langle t^r(m)\rangle = r! \sum_{n\varepsilon V} (\mathbf{L}^{-r})_{nj}\delta_{jm} = r! \sum_{n\varepsilon V} (\mathbf{L}^{-r})_{nm}. \tag{10}$$

Hence the r'th moment is simply related to the r'th power of the inverse of the rate matrix. When L_x is the Fokker–Planck operator, the operator L_x^{-1} can be identified with a Green's function and operators L_x^{-n} are iterates of the Green's function. To establish this fact we expand the Green's function associated with the operator L_x and the boundary conditions of the problem, in terms of the eigenfunctions of L_x. It will then be seen that the resulting expansion is that which arises in the evaluation of $\langle t(y) \rangle$.

The eigenfunctions of $L_x u_n(x)$, are defined by

$$L_x u_n(x) = \lambda_n u_n(x), \tag{11}$$

where it will be assumed that the λ_n are real, distinct, and positive. These conditions are fulfilled in most problems of physical interest, although the theory can be extended to deal with more complicated situations. Since L_x is not necessarily self-adjoint the $u_n(x)$ do not directly form an orthonormal set, but are orthogonal with respect to the eigenfunctions of the adjoint operator $\tilde{L}$ which satisfy[16]

$$\tilde{L} v_n(x) = \lambda_n v_n(x). \tag{12}$$

The relation of orthogonality can be expressed as

$$\int_\Omega u_m(x) v_n(x) dx = \delta_{nm}. \tag{13}$$

One can easily verify by means of this property that the Dirac delta function $\delta(x - y)$ has the representation

$$\delta(x - y) = \sum_{n=0}^{\infty} u_n(x) v_n(y). \tag{14}$$

Since $L_x^{-1} u_n(x) = u_n(x)/\lambda_n$ by application of eq. (8), we have

$$\langle t(y) \rangle = \int L_x^{-1} \sum_n u_n(x) v_n(y) dx = \int \sum_n \frac{u_n(x) v_n(y) dx}{\lambda_n}; \tag{15}$$

and, by the same argument

$$\langle t^r(y) \rangle = r! \int \sum_n \frac{u_n(x) v_n(y) dx}{\lambda_n^r}. \tag{16}$$

One can now verify that the expression for $\langle t(y) \rangle$ is an integral over the Green's function, $G(x,y)$, associated with L_x, and that

$\langle t^r(y)\rangle$ can be written in terms of iterates of the Green's function. The Green's function, G(x,y), associated with the operator L_x is the solution to

$$L_x G(x,y) = \delta(x - y), \tag{17}$$

i.e., it is the continuous analogue of the matrix inverse. If one expands G(x,y) in a series of eigenfunctions associated with L_x:

$$G(x,y) = \sum_n g_n u_n(x), \tag{18}$$

and uses the representation of eq. (14) in eq. (17), it is found that $g_n = v_n(y)/\lambda_n$ or

$$G(x,y) = \sum_n \frac{u_n(x)v_n(y)}{\lambda_n}. \tag{19}$$

A comparison of eqs. (15) and (19) shows that

$$\langle t(y)\rangle = \int G(x,y)dx. \tag{20}$$

Iterates of G(x,y) are defined by

$$G_{n+1}(x,y) = \int G_n(x,z)G(z,y)dz \tag{21}$$
$$G_1(x,y) = G(x,y).$$

The expansion in terms of eigenfunctions of L or $G_n(x,y)$ reads

$$G_n(x,y) = \sum_m \frac{u_m(x)v_m(y)}{\lambda_m^n}, \tag{22}$$

as may readily be confirmed from eqs. (19) and (21). Hence $\langle t^r(y)\rangle$ can also be written

$$\langle t^r(y)\rangle = r! \int G_r(x,y)dx. \tag{23}$$

The expansions of eqs. (10) and (22) are analogues because of the formal relation between the matrix inverse and Green's functions.

So far our results have taken the form of a reduction of a problem stated in probabilistic terms to a purely computational problem. In practice, the applications treated in the literature contain further restrictions on the form of the operator L_x, so that analytic results are possible. In the case of a master equation defined over a discrete set of states it is most often assumed that L represents a nearest-neighbor system, that is $L_{ij} = 0$ for $|i - j| > 1$. A

typical example of this is the Montroll–Shuler model of the dissociation of a diatomic molecule, in which the elements of L are

$$L_{j,j+1} = -\kappa(j+1)e^{-\Theta}, \quad L_{j,j-1} = -\kappa j,$$
$$\text{and} \qquad L_{ii} = L_{j,j-1} + L_{j,j+1}, \tag{24}$$

where κ is a rate parameter, and $\Theta = h\nu/(kT)$ where ν is the characteristic oscillator frequency.[2] It is possible to derive formulae for the $\langle t^r(m)\rangle$ in closed form for these nearest-neighbor systems. Let us consider, as an example, a derivation of the formula for $\langle t(m)\rangle$ when states 0, 1, 2, . . ., N are non-reactant but state N + 1 is a reactant state. We can first observe that we need only calculate $\langle t(0)\rangle$ since if $T_{0,j}$ is the random variable representing the time for the system to reach state j for the first time starting from state 0, it follows from the assumption of a nearest-neighbor system that

$$T_{0,N+1} = T_{0,m} + T_{m,N+1}. \tag{25}$$

That is to say, since every state must necessarily be traversed in passing from state 0 to state N + 1, the total first passage time is made up of the time to reach state m for the first time plus the time to reach state N + 1 for the first time starting from state m. If we let $\langle t_k\rangle$ denote the mean first passage time for getting from state 0 to state k, eq. (25) implies that

$$\langle t(m)\rangle = \langle t_{N+1}\rangle - \langle t_m\rangle, \tag{26}$$

so that we need only calculate a formula for $\langle t(0)\rangle$ with an arbitrary upper reaction level.

In order to calculate $\langle t(0)\rangle$ most expeditiously we will start, not from the general formulation of eq. (10), but rather from eq. (1) which in the present case can be written:

$$\begin{aligned}
\dot{p}_0 &= L_{10}p_1 - L_{01}p_0 \\
\dot{p}_1 &= L_{01}p_0 - (L_{10} + L_{12})p_1 + L_{21}p_2 \\
\dot{p}_2 &= L_{12}p_1 - (L_{21} + L_{23})p_2 + L_{32}p_3 \\
&\cdot \qquad\qquad \cdot \\
&\cdot \qquad\qquad \cdot \\
&\cdot \qquad\qquad \cdot \\
\dot{p}_N &= L_{N-1,N}p_{N-1} - (L_{N,N-1} + L_{N,N+1})p_N,
\end{aligned} \tag{27}$$

where it is to be understood that $p_j(0) = \delta_{j0}$.

[2]

Since $p_V(t) = p_0(t) + p_1(t) + \cdots + p_N(t)$, eq. (6) indicates that

$$\langle t(0)\rangle = \int_0^\infty [p_0(t) + p_1(t) + \cdots + p_N(t)]dt; \tag{28}$$

or, introducing the Laplace transforms $p_j^*(s) = \int_0^\infty e^{-st}p_j(t)dt$, we can also write

$$\langle t(0)\rangle = \sum_{j=0}^{N} p_j^*(0). \tag{29}$$

It is in this form that the calculation becomes most convenient. The Laplace transform of eq. (27) with $s = 0$ is

$$\begin{aligned} &L_{01}p_0^*(0) = L_{10}p_1^*(0) + 1 \\ &(L_{10} + L_{12})p_1^*(0) = L_{01}p_0^*(0) + L_{21}p_2^*(0) \\ &\quad\vdots \qquad\qquad\qquad \vdots \\ &(L_{N,N-1} + L_{N,N+1})p_N^*(0) = L_{N-1,N}p_{N-1}^*(0). \end{aligned} \tag{30}$$

These may be solved recursively to yield

$$p_j^*(0) = \theta_j p_0^*(0) - \eta_j, \tag{31}$$

where

$$\theta_0 = 1,\ \theta_j = \frac{L_{01}L_{12}L_{23}\cdots L_{j-1,j}}{L_{10}L_{21}L_{32}\cdots L_{j,j-1}} \tag{32}$$

$$\eta_0 = 0,\ \eta_j = \frac{1}{L_{j,j-1}}\left[1 + \frac{L_{j-1,j}}{L_{j-1,j-2}} + \frac{L_{j-1,j}L_{j-2,j-1}}{L_{j-1,j-2}L_{j-2,j-3}} + \cdots + \frac{L_{j-1,j}L_{j-2,j-1}\cdots L_{12}}{L_{j-1,j-2}L_{j-2,j-3}\cdots L_{10}}\right].$$

Eq. (31) is derived from the first N lines of eq. (30): if we now substitute eq. (31) into the last line of eq. (30) we obtain an expression for $p_0^*(0)$:

$$p_0^*(0) = \eta_{N+1}/\theta_{N+1}. \tag{33}$$

Thus the mean first passage time is given by

$$\langle t(0)\rangle = \frac{\eta_{N+1}}{\theta_{N+1}}\sum_{j=0}^{N}\theta_j - \sum_{j=0}^{N}\eta_j. \tag{34}$$

In a similar fashion it can be shown that if states 0 and N + 1 form absorbing barriers (that is, the reaction ends when either state is reached) the mean first passage time conditional on the initial state's being r is

$$\langle t(r)\rangle = \frac{\eta_{N+1}}{\theta_{N+1}} \sum_{j=0}^{N} \theta_j - \sum_{j=r+1}^{N} \eta_j. \tag{35}$$

For particular models which are appropriately described by the nearest-neighbor approximation the sums indicated in eqs. (32) and (34) may be rather simple to evaluate. For example, in the Montroll–Shuler treatment of dissociation characterized by the transition rates of eq. (24) it is easily verified that the parameters θ_j and η_j are, respectively:

$$\theta_j = e^{-j\theta},$$
$$\eta_j = \frac{1}{k}\left(\frac{1}{j} + \frac{e^{-\theta}}{j-1} + \frac{e^{-2\theta}}{j-2} + \cdots + \frac{e^{-(j-1)\theta}}{1}\right); \tag{36}$$

so that the mean first passage time to reach state N + 1 in the case of a single reactive state is

$$\langle t(0)\rangle = \frac{1}{k} e^{(N+1)\theta}\left(\frac{1}{N+1} + \frac{e^{-\theta}}{N} + \frac{e^{-2\theta}}{N-1} + \cdots + \frac{e^{-N\theta}}{1}\right)\left(\frac{1-e^{-(N+1)\theta}}{1-e^{-\theta}}\right)$$
$$- \frac{1}{k(1-e^{-\theta})}\left[1 - e^{-N\theta} + \frac{1}{2}(1-e^{-(N-1)\theta}) + \frac{1}{3}(1-e^{-(N-2)\theta})\right.$$
$$\left. + \cdots + \frac{1}{N}(1-e^{-\theta})\right] \tag{37}$$
$$= \frac{1}{k(1-e^{-\theta})} \sum_{j=1}^{N+1} \frac{e^{j\theta}-1}{j}.$$

One can derive expressions for higher moments of the first passage time by following the same line of proof as above. A general treatment of the theory of equations of the form of eq. (27), i.e., with nearest-neighbor transitions only, has been developed by Ledermann and Reuter,[17] and by Karlin and MacGregor.[18] Their results include a general solution to eq. (27) in

terms of recursively defined orthogonal polynomials. In particular, Karlin and MacGregor are able to discuss the statistics of the first passage time problem in terms of the orthogonal polynomials appropriate to the particular set of equations. With their results it is possible to derive expressions for moments of the first passage time rather easily, but I have chosen to omit a discussion of the orthogonal polynomial technique from this article because the moments can be obtained directly. It would be of considerable interest to have results as simple as those of eqs. (34) and (35) for systems not restricted to the nearest-neighbor type, as there are indications[19] that the nearest-neighbor theory does not give results of the right order of magnitude for dissociation times.[1]

III. FIRST PASSAGE TIME AND THE FOKKER–PLANCK EQUATION

We have obtained a general formula for moments of the first passage time in terms of the Green's function of the Fokker–Planck operator. This formulation is useful for problems involving multidimensional geometries. The one-dimensional case can be solved in detail for moments of the first passage time. This is not surprising since the one-dimensional problem is the continuous analogue of the nearest-neighbor models just discussed. We shall present results for the one-dimensional case. These are due originally to Pontryagin, Andronow, and Witt,[20] although special cases were treated earlier by Schrödinger. Recent contributions to the mathematical theory have been made by Darling and Siegert.[21] Jackson and his collaborators have made extensive use of this theory in certain polymer problems.[9,22,23]

In what follows we use the mathematical terminology "absorbing" or "reflecting" barrier to describe the properties of a designated point or surface. A surface is said to be absorbing if it forms a boundary between V and $\bar{V}$, that is, if the process terminates when X(t) reaches a point of the surface. A surface is called reflecting if, when X(t) reaches a point of the surface, it is automatically transferred to a point in the interior of V. In the present article we consider only the case of infinitesimal reflection, i.e., when X(t) is transferred to an infinitesimal neighborhood of the point of impingement.

We begin by considering the one-dimensional case in which $X(t)$ is constrained to lie between $x = 0$ and $x = A$. It will be assumed that $x = A$ is always an absorbing point and $x = 0$ is either reflecting or absorbing.

The probability density for the position of $X(t)$ satisfies eq. (1) with L_x given in eq. (2). Theoretically one can find statistical properties of the first passage time by solving the Fokker–Planck equation for $p(x,t)$ with appropriate boundary conditions. However, it proves considerably more convenient to derive an equation for a function $\phi(x,t)$ defined to be the probability that the first passage time is less than t, given that $X(0) = x$. If $W(y,dt|x)dy$ is the probability that $y \leq X(dt) \leq y + dy$, given that $X(0) = x$, then we may write the equation

$$\phi(x,t + dt) = \int_0^A W(y,dt|x)\phi(y,t)dt, \tag{38}$$

which expresses the fact that a transition $x \to (y,y + dy)$ took place in time dt, and the new position can be regarded as a starting point for the process. The next step is to expand $\phi(y,t)$ in a Taylor series around the point x and substitute into the last equation. This leads to

$$\begin{aligned}\phi(x,t + dt) = \phi(x,t) \int_0^A W(y,dt|x)dy \\ + \frac{\partial\phi(x,t)}{\partial x}\int_0^A (y - x)W(y,dt|x)dy \\ + \frac{1}{2}\cdot\frac{\partial^2\phi(x,t)}{\partial x^2}\int_0^A (y - x)^2W(y,dt|x)dy + \ldots\end{aligned} \tag{39}$$

The Fokker–Planck equation is derived on the assumption that

$$\lim_{dt\to 0}\frac{1}{dt}\int_0^A (y - x)^nW(y,dt|x)dy = 0 \tag{40}$$

for $n \geq 3$. On this assumption, eq. (39) implies that $\phi(x,t)$ is the solution to

$$\frac{\partial\phi}{\partial t} = \frac{a_2(x)}{2}\frac{\partial^2\phi}{\partial x^2} + a_1(x)\frac{\partial\phi}{\partial x}, \tag{41}$$

where the $a_j(x)$ are infinitesimal transition moments

$$a_j(x) = \lim_{dt\to 0} \frac{1}{dt} \int_0^A (y - x)^j W(y,dt|x)dy. \tag{42}$$

The boundary conditions for eq. (41) are $\phi(A,t) = 1$ and $\phi(0,t) = 1$ for $x = 0$ an absorbing point, or $\dfrac{\partial\phi(0,t)}{\partial x} = 0$ for $x = 0$ a reflecting point. A comprehensive discussion of requirements on $a_2(x)$ to ensure a finite first passage time has been given by Feller.[24] For all problems of physical interest there is no difficulty with this point since $a_2(x)$ is strictly positive and bounded away from zero. In dimensions greater than one, it is possible to derive the equation

$$\frac{\partial\phi}{\partial t} = \sum_i a_i \frac{\partial\phi}{\partial x_i} + \frac{1}{2}\sum_i\sum_j b_{ij} \frac{\partial^2\phi}{\partial x_i \partial x_j} \tag{43}$$

for the distribution of first passage time. In this equation the coefficients are defined, analogously to eq. (40), by

$$\begin{aligned} a_i(\mathbf{x}) &= \lim_{dt\to 0} \frac{1}{dt} \int_V (y_i - x_i)W(\mathbf{y},dt|\mathbf{x})d^n\mathbf{y} \\ b_{ij}(\mathbf{x}) &= \lim_{dt\to 0} \frac{1}{dt} \int_V (y_i - x_i)(y_j - x_j)W(\mathbf{y},dt|\mathbf{x})d^n\mathbf{y}; \end{aligned} \tag{44}$$

and it is assumed that higher infinitesimal transition moments are zero. Equation (43) is to be solved under the initial condition $\phi(\mathbf{x},0) = 0$ for $\mathbf{x}$ in V, and $\phi(\mathbf{x},t) = 0$ for $\mathbf{x}$ belonging to an absorbing portion of the boundary between V and $\bar{V}$, and $\partial\phi/\partial n = 0$ for $\mathbf{x}$ belonging to a reflecting part of the boundary, where $\partial/\partial n$ denotes a normal derivative.

Equation (41) together with the boundary conditions on $\phi(x,t)$ enables us to calculate moments fairly readily. The same argument as has led to eq. (6) implies that the j'th moment of the first passage time starting from a point x is expressible as

$$\mu_j(x) = \int_0^\infty t^j \frac{\partial\phi(x,t)}{\partial t}\, dt. \tag{45}$$

If we differentiate eq. (41) with respect to t, multiply by t^j, and integrate over all t, we find that the $\mu_j(x)$ are the solution to the set of equations

$$\begin{aligned} \frac{1}{2}b_2\frac{d^2\mu_j}{dx^2} + b_1\frac{d\mu_j}{dx} &= -j\mu_{j-1} \qquad j = 2, 3, \ldots \\ \frac{1}{2}b_2\frac{d^2\mu_1}{dx^2} + b_1\frac{d\mu_1}{dx} &= -1 \end{aligned} \tag{46}$$

with boundary conditions $\mu_j(A) = 0$ for $x = a$ an absorbing point and $d\mu_j(a)/dx = 0$ for $x = A$ a reflecting point.

The equation for $\mu_1(x)$ can be solved in closed form. The general solution is

$$\mu_1(x) = -2\int_0^x e^{-U(y)}\,dy\int_0^y \frac{e^{U(z)}}{b_2(z)}\,dz + C_1\int_0^x e^{-U(y)}\,dy + C_2, \tag{47}$$

where U(x) is defined by

$$U(x) = 2\int_0^x [b_1(y)/b_2(y)]dy. \tag{48}$$

When both boundaries are absorbing,

$$C_1 = 2\int_0^A e^{-U(y)}\,dy\int_0^y [e^{U(z)}/b_2(z)]dz \Big/ \int_0^A e^{-U(y)}\,dy \tag{49}$$

and $\qquad C_2 = 0;$

and when $x = A$ is absorbing and $x = 0$ reflecting we have

$$\begin{aligned} C_1 &= 0 \\ C_2 &= 2\int_0^A e^{-U(x)}\,dx\int_0^x [e^{U(y)}/b_2(y)]dy. \end{aligned} \tag{50}$$

Formulae for higher moments can be derived recursively from eq. (46), with $\mu_1(x)$ given by eq. (47).

The simplest illustration of the use of these formulae is in terms of simple Brownian motion in one dimension for which $a_1(x) = 0$

and $a_2(x) = 2D$ with D the diffusion constant. The equation for the mean first passage time reduces to $\mu_1'' = -1/D$. If $x = 0$ and $x = A$ are both absorbing, then the expression for mean first passage time is

$$\mu_1(x) = \frac{1}{2D} x(A - x). \tag{51}$$

It is instructive to calculate the statistical properties of one dimensional Brownian motion in a constant force field. Let us consider the case of a semi-infinite interval $(0,\infty)$ with absorption at $x = 0$. The coefficients in eq. (41) are $a_1(x) = -v$ and $a_2(x) = 2D$, where v is assumed to be a constant. The expression for $\mu_1(x)$ is found to be

$$\mu_1(x) = x/v, \tag{52}$$

independent of diffusion effects. The diffusion constant D does, however, appear in the expression for $\mu_2(x)$. An equation for the distribution of absorption times can be written, following eq. (41), as

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2} - v \frac{\partial \phi}{\partial x}, \tag{53}$$

subject to $\phi(x,0) = 0$ for $x > 0$ and $\phi(0,t) = 1$. The solution to this equation is

$$\phi(x,t) = \frac{x}{\sqrt{\pi D}} \int_0^t \frac{dt}{t^{3/2}} \exp\left[-\frac{1}{4Dt}(2x - vt)^2\right], \tag{54}$$

as given by Schrödinger.[5]

First passage time problems in spaces of dimension greater than one require a simple geometry if useful information is to be obtained in closed form. Thus, solutions for the distribution function of first passage times and the moments are readily obtained for force-free Brownian motion in cylinders or spheres, and between parallel plates when these form the absorbing boundaries.[25,26] More complicated geometries may require purely numerical techniques in the solution of associated first passage time problems.

An interesting example of the use of first passage time techniques in chemical physics is provided by Lifson and Jackson's attempt[9] to explain long association times of sodium ions and

polymer macroions observed in transference experiments for polyelectrolytes. Their model is that of the Brownian motion of a counterion in the electrostatic field of a polyelectrolyte molecule. The simplest way to pose the problem in detail is to suppose that we have two bounding planes of $\pm X$. Within this region is a series of equidistant parallel charged planes at $x = 2jL$, $j = -n, -n+1, \ldots n-1, n$ where $X = 2nL$. Lifson and Jackson then go on to calculate the expected time for an ion initially at $x = 0$ to reach a boundary plane. The force on an ion of charge e will be written $\mathbf{F} = -e\nabla\Psi$. It is convenient to define a reduced potential $\phi = e\Psi/(kT)$. The equation for the mean first passage time for a particle performing Brownian motion in a force field derivable from a potential is

$$D\nabla^2\mu_1 + (1/\gamma)\mathbf{F}\cdot\nabla\mu_1 = -1, \tag{55}$$

where $\mathbf{F}$ is the force and γ is the hydrodynamic friction constant. Substituting the expression for $\mathbf{F}$ in terms of Ψ into this equation, and making use of the Einstein relation $D = kT/\gamma$, we find that eq. (55) can be rewritten

$$\nabla\cdot(e^{\phi}\nabla\mu_1) = -e^{\phi}/D \tag{56}$$

Since the system is homogeneous on a macroscopic scale, we might expect that the diffusion process is characterized by a diffusion constant D^* which depends on D and the local electrostatic field of the polyelectrolyte molecule. The object of Lifson and Jackson's analysis was to calculate D^* for a model system. One solves for D^* by calculating $\mu_1(0)$ and equating it to the expression

$$\mu_1(0) = X^2/(2D^*), \tag{57}$$

which is the expression relevant for the case of field-free Brownian motion. The average time $\mu_1(0)$ is given by

$$\mu_1(0) = \frac{1}{D}\int_0^x du\, e^{-\phi(u)}\int_0^u e^{\phi(v)}\, dv. \tag{58}$$

To obtain an expression for D^* we introduce the notation

$$\langle e^{\phi}\rangle = \frac{1}{2L}\int_0^{2L} e^{\phi(y)}dy. \tag{59}$$

Since $\phi(x)$ is periodic with period 2L, far from the boundaries, eq. (58) can be rewritten

$$\mu_1(0) = \frac{1}{D}\sum_{m=0}^{n-1}\int_{2mL}^{2(m+1)L} du\, e^{-\phi(u)}\int_0^u dv\, e^{\phi(v)}$$

$$= \frac{1}{D}\sum_{m=0}^{n-1}\int_{2mL}^{2(m+1)L} du\, e^{-\phi(u)}\left[2mL\langle e^{\phi}\rangle + \int_{2mL}^{u} dv\, e^{\phi(v)}\right]$$

$$= \frac{1}{2D}(2nL)^2\langle e^{-\phi}\rangle\langle e^{\phi}\rangle = \frac{X^2}{2D}\langle e^{\phi}\rangle\langle e^{-\phi}\rangle \qquad (60)$$

A comparison between eqs. (57) and (60) yields the result

$$D^* = D/(\langle e^{\phi}\rangle\langle e^{-\phi}\rangle) \qquad (61)$$

for the particular one-dimensional model under consideration. The Cauchy–Schwartz inequality can be used to show that $\langle e^{\phi}\rangle\langle e^{-\phi}\rangle \geq 1$, so that

$$D^* \leq D. \qquad (62)$$

Jackson and Coriell[22] have shown that this inequality holds in any number of dimensions. Lifson and Jackson concluded from their study that the retardation of drift of counterions in polyelectrolyte solutions might be accounted for by their entrapment in the electrostatic fields of the macroions.

Another problem related to the first passage time problem is that of calculating the probability of absorption by a particular one of a set of absorbing barriers. For example, in one dimension we can consider the probability of termination at $x = 0$, given that $x = 0$ and $x = A$ both offer the possibility of absorption. Such a mathematical problem finds application in elucidation of the theory of competitive rate processes. If the transfer of energy can be described in terms of a stochastic process, e.g., if the energy distribution obeys a Fokker–Planck equation, then the probability of one of a set of outcomes can be calculated by the technique to be described.

Let us first consider the one-dimensional case in which absorption can occur at either $x = 0$ or $x = A$. Let $\phi_0(x)$ be the probability of absorption at $x = 0$ given a starting point x. We define a function $\phi_0(x,t)$ to be the probability of absorption at

$x = 0$ before time t, given the starting point x. The desired probability $\phi_0(x)$ is then

$$\phi_0(x) = \lim_{t \to 0} \phi_0(x,t). \tag{63}$$

The function $\phi_0(x,t)$ is a solution to eq. (41), the derivation being the same as given above. However, the boundary conditions are now to be changed to

$$\phi_0(0,t) = 1, \phi_0(A,t) = 0. \tag{64}$$

Setting $\partial\phi_0/\partial t = 0$ in eq. (41), we see that $\phi_0(x)$ is the solution to

$$\frac{1}{2} a_2(x) \frac{d^2\phi_0}{dx^2} + a_1(x) \frac{d\phi_0}{dx} = 0 \tag{65}$$

with boundary conditions $\phi_0(0) = 1$, $\phi_0(A) = 0$. The solution to eq. (65) under these circumstances is

$$\phi_0(x) = \int_x^A e^{-U(y)} dy \Big/ \int_0^A e^{-U(y)} dy, \tag{66}$$

where U(x) is defined in eq. (48). For Brownian motion in a constant force field $\phi_0(x)$ is found to be

$$\phi_0(x) = \frac{1 - e^{-(v/D)(A-x)}}{1 - e^{-(vA/D)}}. \tag{67}$$

In the limit $v \to 0$ this reduces to $\phi_0(x) = 1 - (x/A)$, as is to be expected. The theory for more complicated geometries is similar. If the boundary between V and $\bar{V}$ is broken up into n segments $S_1, S_2, \ldots, S_n$ the probability of absorption by a particular segment S_j, $\phi_j(x)$, satisfies eq. (43) with $\partial\phi_j(x)/\partial t = 0$ and the boundary conditions $\phi_j(x) = 0$ for x in

$$S_1, S_2, \ldots, S_{j-1}, S_{j+1}, \ldots, S_n, \text{ and } \phi_j(\mathbf{x}) = 1 \text{ for } \mathbf{x} \text{ in } S_j.$$

There are many further applications of first passage time problems in chemical physics, particularly in the study of polymers.[27] Some of these involve first passages defined on Markov chains, a subject that has not been touched in the present article. However, the theory is similar to that developed here. The interested reader should refer to Kemeny and Snell's book[28] for a discussion of first passage time problems in discrete time.

Although it might appear at first glance that such problems would be completely unphysical, they have applications in polymer physics, where the analogue of time units are bond lengths of monomers.

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REACTION KINETICS IN HYPERSONIC FLOWS*

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SYMBOLS

A	Cross-sectional area in equations
A,B,C	Schematic chemical symbols in reactions
c_j	Mass concentration of j'th species
d	Sphere diameter
e	Internal energy
h	Enthalpy
$\mathbf{J}_j$	Diffusion flux of j'th species
M	Mach number
m_j	Molecular weight of j'th species
p	Pressure
Q	Heat flux

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$\mathbf{q}$	Velocity
$\mathbf{R}_0$	Gas constant
T	Temperature
t	Time
u	Streamwise velocity component
w_{ij}	Mass production rate of j'th species from i'th reaction per unit volume
ξ	Streamwise coordinate
ρ	Density
τ	Shear stress

Subscripts:

i	Reaction index
j	Species index

I. INTRODUCTION

A host of technical problems have come with man's desire to fly himself and his instruments at several times the speed of sound. Many of these revolve around the new properties of the flight medium brought about by its changing chemical composition. Dissociation and ionization arise from dissipative processes in shock waves, and frictional heating occurs in boundary layers. Hence, chemical physics becomes a central consideration in an understanding of the flow properties.

In view of this fusion of chemical and aerodynamic problems, this paper will review the ways in which chemical reactions couple with flows; and two specific examples will be provided. We shall use the governing laws in abbreviated mathematical form and, in the examples, shall describe and interpret experimental investigations. We must, however, first define some terms and also some quantitative regimes of flow chemistry.

Let us consider the meaning of the word "hypersonic." Physical and mathematical ways of thinking about compressible flows are classified by the ratio of typical flow speed to local sound speed, i.e., the Mach number. The hypersonic regime is characterized by a strong transverse disturbance field set up by the flight object within the ambient medium. Specifically, these disturbances are non-linear even for slender bodies. In supersonic flight, however, the cross-wise fluid motion pattern can be treated in the acoustic

or weak-wave approximation for thin bodies. Although this idea does not delineate a definition, it pinpoints the significant dynamic qualities of hypersonic flow.

For typical bodies of revolution under consideration for high-speed flight, the hypersonic regime begins in the range $5 < M < 10$. The lower edge of this range involves surface-heating problems even at rather high altitudes (tens of kilometers) for steady flight, but the flow chemistry becomes significant only at the upper limit of this range. A criterion for including chemical reaction is best characterized by the ratio of bond energy to flow kinetic energy. This ratio need only be 10^{-1} for substantial dissociation according to the mass-action law. Dissociation of the oxygen of air becomes considerable at about 3 km/sec, which gives normal shock temperatures in the neighborhood of 3,000°K. We shall limit our discussion to terrestrial atmospheric flight, so that the maximum velocity under consideration will be about 8 km/sec. Within such a regime shock temperatures of 3,000–9,000°K would be expected after the gas has equilibrated. Corresponding peak temperatures in boundary layers on cold walls of slender conical bodies are somewhat greater than one-half of the shock temperatures given. If the discussion is further limited to continuum flows, the total flow-field particle densities range from 10^{13} to 10^{18} cm^{-1}, corresponding to flight altitudes between 30 and 100 km.

II. COUPLING BETWEEN REACTION KINETICS AND FLUID DYNAMICS

A. Governing Equations

To demonstrate how chemical change interacts with flow phenomena, it is necessary to consider the laws governing the system. These laws can be placed in two categories: conservation equations and constitutive relationships.

Beginning with the species equation, let us examine the first category of laws by writing them schematically. The mass concentration of j'th species c_j is governed by the equation:

$$\frac{\partial c_j}{\partial t} + \mathbf{q} \cdot \nabla c_j = -\frac{1}{\rho}\left(\nabla \cdot \mathbf{J}_j - \sum_i w_{ij}\right), \tag{1}$$

where $\mathbf{q}$ is mean flow velocity, t is time, ρ is density, $\mathbf{J}_j$ is transport flux ($\rho c_j \mathbf{q}_j$), and w_{ij} is the net mass production rate of species j from reaction step i per unit volume. The symbol $\mathbf{q}_j$ represents the total velocity of the j'th species. Equation (1) tells us that the local plus the convective rate of concentration change arises from the combined effects of diffusion and reaction.

Overall mass conservation is expressed by

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{q}) = 0. \tag{2}$$

This is simply a statement that the local rate of change of mass in a small control volume is balanced by the net outward mass flux from that element.

The total momentum equation is written as:

$$\frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} \cdot \nabla \mathbf{q} = -\frac{1}{\rho} (\nabla p - \nabla \cdot \tau) \tag{3}$$

in which p denotes static pressure and τ is the shear stress tensor. Equation (3) is a statement of Newton's second law; i.e., the total rate of momentum change is equal to the sum of the normal and the shear force.

Finally, the global conservation of energy is described by the equation

$$\frac{\partial}{\partial t}\left(h + \frac{1}{2}|\mathbf{q}|^2\right) + \mathbf{q} \cdot \nabla\left(h + \frac{1}{2}|\mathbf{q}|^2\right) = -\frac{1}{\rho}\left[\nabla \cdot Q - \frac{\partial \rho}{\partial t} - \nabla \cdot (\mathbf{q} \cdot \tau)\right], \tag{4}$$

where h is the static enthalpy (the sum of an internal energy term e and a steady-flow work term $p\rho^{-1}$). The symbol Q denotes the heat flux by molecular transport. Since h includes chemical energy, the quantity under the operator on the left-hand side of equation (4) is the total energy of significance to a flow system. This is sometimes called the stagnation enthalpy. Its local and convective rates of change are the sum of heat transfer, unsteady-flow work, and viscous dissipation effects as given in the right-hand side of equation (4).

The constitutive laws relate quantities of the thermodynamic state:

$$p = \rho \mathbf{R}_0 T \sum_j (c_j/m_j), \tag{5}$$

and the caloric state:

$$h = \sum_j c_j h_j, \tag{6}$$

where m_j is the molecular weight of the j'th species and h_j is the enthalpy of the j'th species, including energy of formation.

Other constitutive equations deal with the transport and production terms on the right-hand sides of the conservation laws. For high-temperature gas dynamics we usually use a temperature-dependent transport coefficient relating the flux and the gradient of a quantity. Specifically, Fickian diffusion, Newtonian stress–strain rate, and Fourier heat-conduction laws are often employed in the Navier–Stokes approximation.

Derivations of the conservation and constitutive laws can be found in a number of standard works.[1–4]

The focus of attention for our purposes is the role of the constitutive law for species production, $w_{ij}(c_j, \rho, T)$. The typical element of the chemical production term is expressed in the usual chemical kinetic language involving a temperature-dependent rate coefficient times the proper product of concentrations.

B. Transformation to Intrinsic Coordinates and Neglect of Transport Effects

To highlight the reaction kinetic coupling, we shall immediately restrict our considerations to steady flow without transport effects. This permits a transformation to a coordinate system which is intrinsic to flows. This system has one coordinate direction aligned with the velocity vector and the other normal to the velocity vector. We can imagine a flow field built up of elementary channel flows aligned in the streamwise direction. Conditions are practically uniform across a right section of each channel if the width is chosen to be very small. Such channels are called streamtubes because their "walls" are made up of streamlines. In a steady flow, streamlines coincide with particle trajectories. Thus, each streamtube can be treated as a quasi-one-dimensional flow obeying any of several prescribed boundary

conditions; e.g., area distribution $A(\xi)$, pressure distribution $p(\xi)$, density distribution $\rho(\xi)$, or velocity distribution $u(\xi)$, where ξ is the distance measured in the streamwise direction. The new geometry may be sketched as shown in Fig. 1.

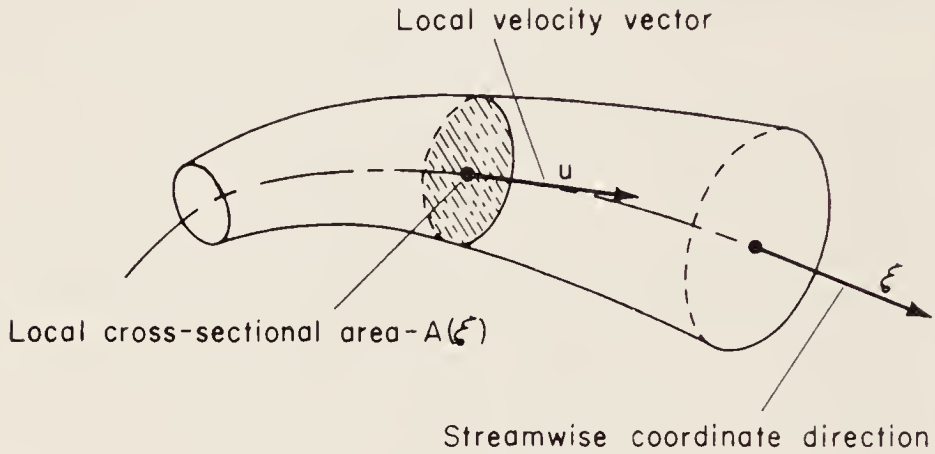

Fig. 1. Streamtube geometry.

Under the set of restrictions stated above and the coordinate transformation adopted, the governing equations become:

Species:

$$\rho u \frac{dc_j}{d\xi} = \sum_i w_{ij} \tag{7}$$

Mass:

$$\frac{d}{d\xi}(\rho u A) = 0 \tag{8}$$

Momentum:

$$\rho u \frac{du}{d\xi} = -\frac{dp}{d\xi} \tag{9}$$

Energy:

$$\frac{d}{d\xi}\left(h + \frac{1}{2}u^2\right) = 0 \tag{10}$$

The constitutive relationships are invariant under the changes made.

C. Types of Reaction Kinetic Coupling

Now we can examine the nature of the interaction between fluid flow and kinetics with the aid of the reduced system of equations. The conclusions drawn will apply equally to the more complex counterpart system of equations given initially.

Chemistry is connected to flow processes through w_{ij}, the production function in equations (1) and (7) which depends on temperature, density, and generally all of the mass concentrations. The nature of the coupling can be typified by the extent to which w_{ij} affects gross behavior of the flow field. We shall consider two types of coupling: *active* and *passive*.

In the simpler case, that of *passive coupling*, the species concentrations of interest have negligible influence on the gross energy distribution in the flow. Put another way, the magnitude of the reaction rate in question does not strongly affect the temperature, density, and velocity fields. The passively coupled reaction is imbedded in a "heat bath" having externally imposed dynamical conditions. It responds, but does not feed back significant changes to the flowing medium.

The *active coupling* of a reaction stands in contrast to the situation just described. As a defining criterion, a species participating in an actively coupled reaction has a large $c_j h_j$ contribution in the sum on the right-hand side of equation (6). Changes in c_j are first reflected as changes in velocity in equation (10) through h, the mixture enthalpy. Secondarily, they also have an effect on pressure or density through the thermodynamic state law, equation (5). From these points of departure the effects propagate into the mass and momentum equations. Since one species can generally feed into several reaction steps, coupling will occur rather directly among the species conservation laws.

A typical example of strong coupling occurs in a highly dissociated gas which expands rapidly from an initially equilibrated state. Sudden cooling and lowering of density depress the dissociation rate markedly, and the recombination process lags in its attempt to restore equilibrium. A failure to release latent energy of molecule formation enhances the cooling and puts the system still farther out of equilibrium. If expansion is fast enough, the recombination lag grows indefinitely and the composition becomes

frozen. Thus, a certain portion of stored energy never finds its way into directed kinetic energy. Here is an example where the freezing process feeds back upon itself in the case of active coupling.

The relaxation zones in a fully dispersed shock wave in a molecular gas provide another rich source of examples of active coupling. Within a few collisions, translation becomes excited, being followed quickly by rotation. Then, as vibrational levels begin filling, dissociation first appears. During the dissociation phase, the gas cools and becomes denser because of energy absorbed in the reaction. Of the two competing effects on dissociation rate, cooling predominates because of the powerful temperature effect, and dissociation becomes ever slower until it is equally opposed by recombination at equilibrium. This interplay complicates the interpretation of experiments on shock-wave kinetics of actively coupled reactions.

III. TYPICAL KINETIC MECHANISMS

Having examined in detail the nature of the coupling, we now turn to the specific rate processes typifying reacting airflows. For the terrestrial flight conditions of interest to us here (velocity 3–8 km/sec, altitude 30–100 km) reactions involving neutral species are usually actively coupled, while those involving charged species are passively coupled to the flow. The former include direct dissociation,

$$AB + C \rightleftarrows A + B + C \tag{11}$$

and exchange,

$$AB + C \rightleftarrows AC + B \tag{12}$$

The latter include associative ionization,

$$A + B \rightleftarrows AB^+ + e^- \tag{13}$$

impact ionization of molecules,

$$AB + C \rightleftarrows AB^+ + e^- + C \tag{14}$$

impact ionization of atoms,

$$A + B \rightleftarrows A^+ + e^- + B \tag{15}$$

atom-molecule charge transfer,

$$A^+ + BC \rightleftarrows A + BC^+ \tag{16}$$

collisional detachment,

$$AB^- + C \rightleftarrows AB + e^- + C \tag{17}$$

associative detachment,

$$A + B^- \rightleftarrows AB + e^- \tag{18}$$

and mutual neutralization,

$$AB^+ + CD^- \rightleftarrows AB + CD \tag{19}$$

In considering these reactions for actual cases, it is not necessary to consider all permutations of A, B, and C representing nitrogen and oxygen atoms in airflows. *A priori* quantitative ordering, based on energetic considerations, eliminates very many of the possibilities.

In illustration we shall consider the interpretation of two very different experiments on reaction kinetics in hypersonic flows, namely deionization of air expanding in a Laval nozzle, and electron-density distributions in the near wake of hypersonic body. Both experiments involve measurements of free electron densities in flow systems. It is useful to digress briefly here to explain the choice of the examples. Unlike many investigations involving indirect effects of active coupling (e.g. alteration of pressure or total density distributions by non-equilibrium processes), those selected contain direct observations of the species in question. The advancement of microwave plasma-diagnostic techniques is an important consideration underlying such a choice. The reactions governing electron production and removal are passively coupled so that the "heat-bath" history is determined by a combination of neutral chemistry and fluid dynamics. Finally, both experiments are to a very good approximation free from transport effects. In each case extensive auxiliary experiments were conducted to assure minimal contaminant effects. The first experiment, carried out at Cornell Aeronautical Laboratory, is described in Section IV, and the second, carried out at GM Defense Research Laboratories, in Section V.

IV. ELECTRON-ION RECOMBINATION IN AN EXPANDING CHANNEL FLOW

The supersonic part of a Laval nozzle is characterized by divergent walls. As the gas flows supersonically through such a channel its internal or random kinetic energy is converted into direct kinetic energy. Density and temperature fall monotonically if exit pressure is kept low. When the gas begins its expansion from a dissociated or ionized state, the association reactions eventually fail to keep pace with the changes required to maintain equilibrium, as described in the previous section.

The basis of the channel-flow experiment is a measurement of the free-electron density in the expanding gas. For a known initial condition and channel geometry, the extent of the lag is a measure of the sluggishness of the rate processes. Since detailed descriptions of both the experimental[5] and theoretical[6] methodology appear elsewhere, only the essential features will be covered here.

The gas-dynamic facility in which this experimental work was performed is best described as a short-duration ($\sim$1 msec) high-performance wind tunnel. This configuration has been developed and employed at the Cornell Aeronautical Laboratory for plasma-sheath and hypersonic aerodynamic investigations. The hypersonic nozzle (constituting the flow channel) is supplied by gas processed by the reflected shock wave at the end of a shock tube. The use of statically heated hydrogen driver gas produced pressures in the 10^3 atm regime at temperatures up to 8,000°K in the stagnant-air reservoir feeding the nozzle. The nozzle was carefully designed to produce a clean uniform flow; the flow turned 10° around a wedge which provided centrifugal separation of diaphragm fragments, and a channel geometry designed for gas-dynamic wave cancellation insured parallel uniform flow at the measuring station. Microwave interferometry at 9.375 GHz was employed for measurement of electron density and collision frequency.

Test conditions required for the design of the particular experiment were based on solution of the non-equilibrium airflow in the nozzle. Numerous calculations were carried out on an IBM 704 computer. In order to define a simple rate model needed for inter-

pretation of the results, many of the calculations were repeated with successively truncated kinetic matrices. Initially, 39 reaction steps involving 13 species were used. All but 9 of the steps governed charged species and are described by classes (11) through (19) of the preceding section. A second model omitted negative heavy ions, attachment–detachment reactions (classes 17 and 18), and the neutralization reactions (class 19). This model had 12 species participating in 32 steps. Finally, nozzle calculations were performed with all charged particles omitted except electrons and nitric oxide ions, and all ion reactions omitted except dissociative recombination of NO^+ and e^- (plus its reverse). This third and simplest case included species taking part in 10 reaction steps. Comparisons of electron-concentration decays for the three models showed no measurable distinction. It appeared, therefore, that the simplest treatment contained sufficient detail to describe air ionization under the temperature, pressure and expansion-rate conditions of interest; namely, $T \sim 3{,}000$–$8{,}000°K$, $p \sim 20$–800 atm, and nozzle scale size of 1 cm.

Electron density and collision frequencies were measured at an effective ratio of local area to throat area of approximately 300 for the range of conditions delineated above. Many experimental points were obtained, as reported in ref. 1 and shown in Fig. 2 (reproduced from ref. 5). For reservoir temperatures between 5,000 and 7,000°K, Fig. 2 shows that the experimental values were consistently higher than theoretical curves based on lower bound rates for reaction (13) obtained by Lin *et al.*[7,8] For reservoir pressures of 75–850 atm, the predictions scattered over a bandwidth of approximately a factor of 2. The mean of the data, however, was approximately a factor of 5 higher than that of the predictions.

Several interesting conclusions can be drawn from these findings. Experimental reproducibility was excellent because the pressure insensitivity of the experiments was nearly that predicted. Higher pressure has the compensating effects of raising the overall density (and, hence, the electron density) and depressing the degree of ionization. If the systematic deviation arose from using the incorrect reaction rate in the predictions, complete agreement could be obtained by a downward revision of the electron-ion recombination rate by a factor of 5 (as was verified by further

machine calculations). Since the rate data employed were based on the forward (endothermic) reaction, the conversion into the reverse rate through assumption of detailed balancing may be fallacious.

Low-temperature runs (3,000–4,000°K) showed scatter of an absolute magnitude of about 10^{10} electrons per cm^3, and the high-temperature data were nearly all in excess of 10^{11} electrons per

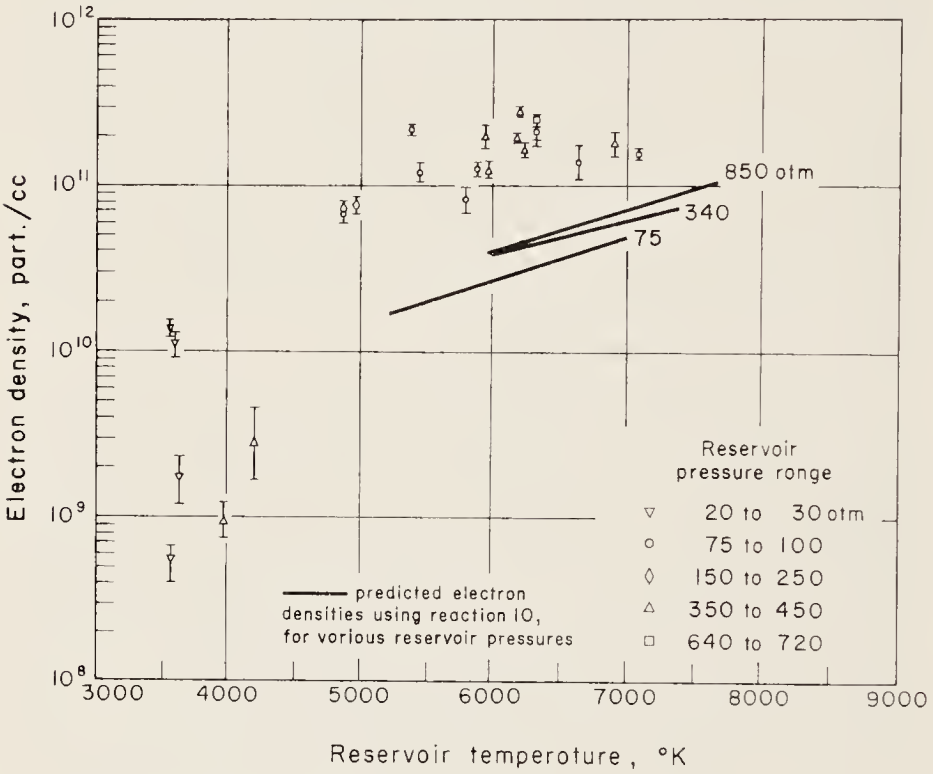

Fig. 2. Electron density at microwave station in shock tunnel nozzle (reproduced from ref. 5 with permission of AGARD–NATO). Reaction 10 refers to dissociative recombination of electrons with nitric oxide ions.

cm^3. This sets an upper limit of about 10 per cent on inaccuracies arising from random variations in impurities from run to run. Careful subsequent tests were run with pure nitrogen, which has a higher effective ionization potential than air, in order to check further the question of impurities either in the test gas or from

transient outgassing. The predicted depression in electron density was recovered experimentally.

All indications pointed to a real kinetic effect rather than a systematic experimental inaccuracy.

The most likely phenomenological explanation involves electron gas energy relaxation. For all calculations the electron temperature was set equal to the gas kinetic temperature. An average electron temperature elevation above average gas kinetic temperature of approximately a factor of 3 is sufficient to explain the results. Appleton and Bray[9] suggested that the force balance between the axial electron pressure gradient and the electric field force driven by collective charge separation constitutes an efficient path for electron gas equilibration even in the absence of collisions; i.e., work done by the electrons against the space charge field removes sufficient energy to maintain equilibrium. Since experimental results showing electron energy freezing were cited in ref. 9, those authors suggested that elecronic heat conduction in the flow direction may prevent the equilibration from occurring. A second explanation offered by the same authors[10] is that the nozzle walls may short-circuit the space charge fields, allowing current build-up which heats the electron gas. Stein *et al.*[11] got results virtually in agreement with those in refs. 7 and 8 for a direct measurement of recombination in an expanded flow. Instead of a metal nozzle as used in the experiment of ref. 5, they used a quartz tube. They claimed, by implication, that forward and reverse rates are related through the equilibrium constant. This development favors the second explanation by Appleton and Bray. Fig. 3 (also reproduced from ref. 5) shows the elevation of electron collision frequencies above expectations as reported in ref. 5. Even employing the kinetic temperature of the throat* failed to match experimental findings at the lower pressures. These results also are consistent with the second explanation.

The apparent anomalies among these experiments can be explained in a reasonable manner. Electron temperature effects

* The static temperature at the nozzle throat is within 10 per cent of the reservoir temperature for all cases considered. Assigning throat temperature to the electron gas gives a high estimate for collision frequency under the assumption of an electron energy freeze occurring early in the flow.

in the recombination experiments may well be responsible for the variations. Proper theoretical treatment of such phenomena probably requires the addition of an electron energy balance to the conservation laws as prescribed in ref. 9.

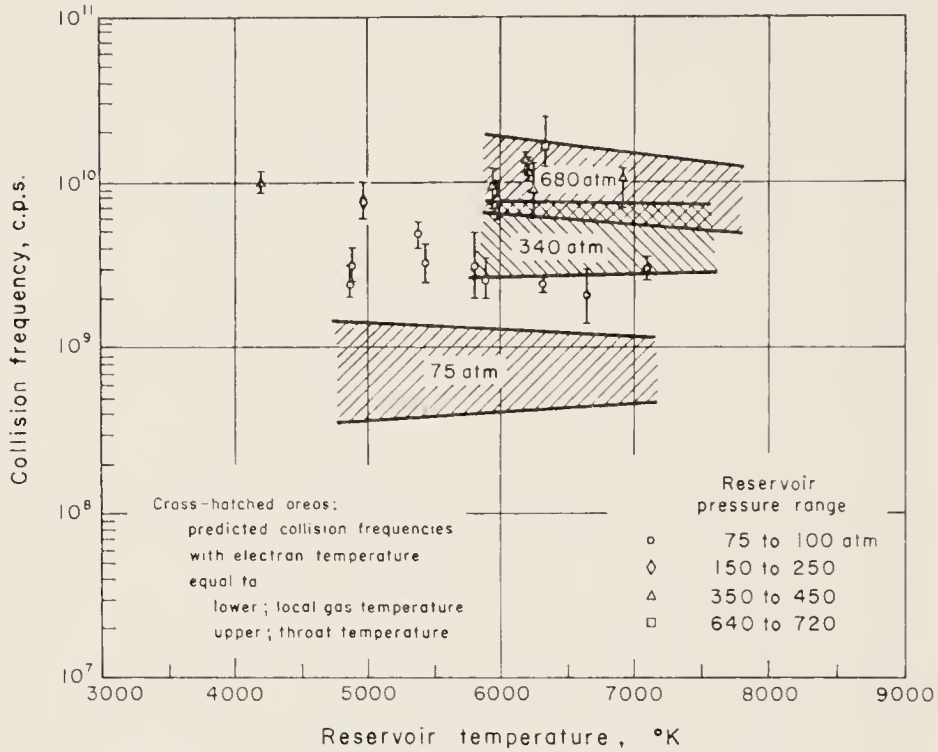

Fig. 3. Electron collision frequency at microwave station in shock tunnel nozzle (reproduced from ref. 5 with permission of AGARD–NATO).

V. IONIZATION IN THE NEAR WAKE OF A SPHERE IN HYPERSONIC FLIGHT*

When a blunt object flies at many times the acoustic speed in the ambient gas, its interaction with the gas is characterized by the oncoming fluid's being blasted aside. The most prominent manifestation of this action is a detached bow shock wave which causes extensive irreversible heating of the gas. In the flight regimes described previously, the heating is sufficient to cause considerable dissociation and ionization of the gas around and

* Much of the reference material for this section was not published at the time of the lecture. Contract reports are recorded in the references.

far behind the body. For bodies which do not ablate or contaminate the flow, the preponderance of ionization in the trail is caused by shock heating. If we consider typical body dimension as centimeters or tens of centimeters in size, the viscous action in the flow is confined to a thin boundary layer on the surface and a slender viscous core in the wake for the first hundred body diameters. The viscous regions are surrounded by a thick layer of hot gas which has first been impulsively compressed and then allowed to expand.

Reaction kinetics in this shock layer first drive in the endothermic direction and then gradually, as the gas cools upon subsequent expansion, try to drive in the exothermic direction. Hence, the interpretation of experimental measurements in the layer must contain all of the ingredients of reversible kinetics mixed with three-dimensional compressible flow.

These observations set the stage for studying the second experiment, the investigation of wake ionization behind a non-ablative sphere flying through pure air. The facility employed for conducting this experiment was the free-flight range at GM Defense Research Laboratories (GM DRL).[12] Here bodies of the order of a centimeter in size are projected from a two-stage hydrogen gun at speeds up to 10 km/sec; free flight is established after the flight model is separated from all solid and gaseous debris that arises on launching. After passing through an explosively actuated shutter valve, the model flies through a cylindrical chamber loaded with a gas at a prescribed pressure and of a prescribed composition. Numerous measurements are made with spectroscopic, radiometric, shadowgraph, schlieren, X-ray, laser photographic, microwave probe, microwave cavity, and radar instrumentation in order to diagnose the condition of the flow field and the integrity of the model. Within rather wide limits, the model geometry, model composition, flight medium, and flight conditions can be varied at will. In the present discussion we shall confine our attention to spherical models, 15 mm in diameter and made of polycarbonate plastic plated with copper. The thickness and preconditioning of the plated surface are chosen to eliminate any effects of ablative contamination for the flight conditions of interest (air at a pressure of 10–100 torr, and a flight velocity of 6.0–7.5 km/sec).

The main instrumentation employed for the experiment is the focused microwave probe.[13] This instrument (which is used in 35-GHz and 70-GHz versions at GM DRL) involves multiple transverse beams of microwave energy focused to about a wavelength in resolution and directed transverse to the flight path. The beams are parallel and are arrayed in a vertical stack perpendicular to the flight line. Each channel effectively acts as an interferometer, yielding phase shift and attenuation information as functions of time (or model position, since the flight dynamics are measured independently). The resolution in space is about one wavelength in size and the sensitivity permits measurements from 10^{10}–10^{12} electrons per cm^3.

The data produced permit the unfolding of both radial and axial electron-density profiles for a single flight test; however, the discussion here will be confined to the electron density integrated transverse to the flight path as determined by a single channel, in principle. (Since the flight line does not always intersect a channel centreline, analysis of multichannel information is nearly always necessary.) Over the past few years, hundreds of flight tests have been conducted over the previously mentioned range of conditions for the model configuration described. This has permitted extensive treatment of the data by cross-plotting and analysis so that a rather good map of integrated electron density has been obtained[14] with an overall uncertainty of a factor of two (owing primarily to test-to-test variations).

Theoretical interpretations are (as with the other experiment) based upon solutions of the coupled kinetic and fluid dynamic laws for the various conditions. The shock layer on the nose of the sphere is solved by using the axisymmetric inverse method beginning with the shock shape and marching radially inward to locate the body surface by mass balance.[15] The final ray of this net is used as a locus of initial conditions for up to 15 streamtubes obeying prescribed pressure distributions. The streamtubes are solved over the region where viscous mixing is of no consequence to the integrated electron density (within 100 body diameters back in the wake). A detailed description of the methodology for synthesizing the flow field can be found in ref. 16.

The kinetic model (defining which species and reactions should be used) was established on the basis of comparisons given in

ref. 5 among successively truncated systems for blunt-body inviscid flows. These calculations were performed at that time (1962) in conjunction with those for the nozzle flows, but experimental verification had not been available until the present. The resultant S × 10 matrix was indentical with that for the nozzle flow. Its use is restricted to the inner part of the shock layer for high-velocity (>5 km/sec) high-altitude (>30 km) flight. Its

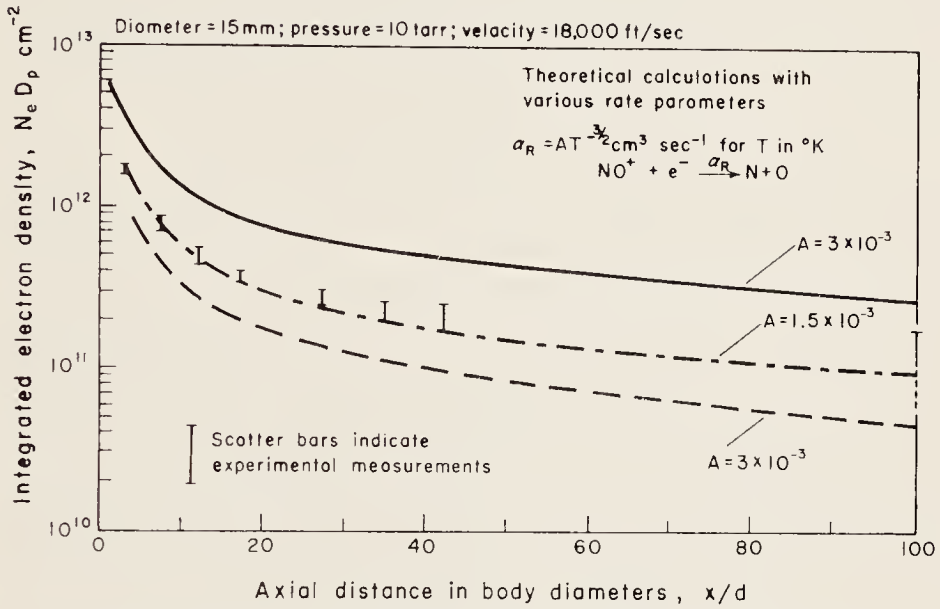

Fig. 4. Near-wake ionization behind non-ablating spheres (diameter 15 mm; pressure 10 torr; velocity 18,000 ft/sec).

validity is further limited to the near wake (less than several hundred diameters) where electron attachment processes play negligible roles in deionization.

The first step in the analysis of the data is establishing a benchmark for the electron-ion recombination rate. This follows the reasoning used in interpreting the channel-flow experimental results. A flight condition centrally located on the pressure scale was chosen for the lower limit of velocity. Calculations were first carried out for the flow field at an ambient air pressure of 10 torr and a flight speed of 5.9 km/sec. Use of the reaction rates suggested in ref. 5 gave a predicted ionization curve approximately 2.5 times greater than the experimental points (see Fig. 4).

Parametric calculations of streamtube flows were performed to study the sensitivity of ionization to each rate constant. It was found that the dissociative recombination of electrons and NO^+ is the dominant process. Next in importance was oxygen dissociation. The remaining reactions had little influence. Since the largest uncertainty was believed to be in the rate of the deionization reaction, the variation in this was chosen to bring the model into accord with experimental observations.

The lowest curve on Fig. 4 shows the result of a ten-fold upward adjustment of the dissociative recombination rate originally used. Finally, it is seen that the computation fits the data well with a rate constant of $1.5 \times 10^{-2}T^{-3/2}$ cm^3 sec^{-1} for $NO^+ + e^- \rightarrow N + O$. Shock-tube measurements,[7,8] it will be recalled, lie between one-fifth and three-fifths of this value. The nozzle experiment indicated an apparent rate of only 4 per cent of this value because of the possible elevation in electron temperature.

Preliminary computations in which the adopted rate constant for velocities up to 6.57 km/sec is used show reasonably good agreement with the experimentally determined velocity-dependence. This is an approximate check on the correctness of the activation energies employed. Other computations for various pressures at a fixed velocity are in progress. The pressure-dependence should give some idea as to the validity of the overall reaction order resulting from the coupled processes.

Without the benefit of such calculations, however, we can still draw some conclusions regarding the order. A systematic series of experiments was conducted for spheres of 5 and 15 mm diameter at a speed of 5.80 km/sec.[17] Within each pair of tests the pressure–diameter product was held constant. Experimental curves of scaled electron density versus scaled distance were coincident for $pd < 750$ torr-mm. This indicates that binary collision chain processes are responsible for ionization processes in the stated regime. From an engineering point of view we see that we can scale the ionization measured in the laboratory up to large vehicles flying in the atmosphere within such limits.

The principles underlying this binary reaction scaling have been discussed[18] and analyzed[19] recently for multicomponent systems. Stated briefly, the scaling requirements are: (1) the flight velocity in the model experiments must equal that of the prototype, and

(2) the product of ambient density and characteristic length must be preserved. If these conditions are satisfied, mass concentration fields will be geometrically similar for bodies of different size when three-body reactions are unimportant. The second condition keeps constant the average number of binary collisions suffered by a molecule in its transit through any given region of the flow. Thus, by experimental inference within the framework of similitude theory we find that production and removal of electrons are dominated by binary collisions for a velocity of 5.80 km/sec and a pressure-diameter product less than 750 torr-mm.

VI. CONCLUDING REMARKS

The coupling of chemical kinetics to fluid dynamics presents a many-faceted problem. For hypersonic conditions, the gross features of the gas dynamics are frequently affected by the rate at which energy goes into and out of chemical modes of storage. This so-called active coupling demands that the complete set of conservation and constitutive laws be considered as an ensemble. Simplifications can be effected for passive coupling where reactions do not feed back measurably into the bulk thermodynamics. Rate equations can be considered separately with the fluid-dynamic behavior introduced as a prescribed heat-bath history.

In an effort to illustrate the state of progress in these areas a very limited, but nevertheless very significant, class of reactions, has been considered here. The ionization processes in the airflows investigated are dominated by a single rate process. This passive process was studied on a background of actively coupled neutral-particle chemistry. The use of currently accepted chemical rates for the active coupling gives a consistent set of results for the ionization process if electron energy is not considered to be in equilibrium for the channel flow. The competition between ohmic heating, vibrational heating, and flow work output of the electron gas has yet to be treated on a quantitative basis.

An emergent fact is our relatively precise understanding of the fluid dynamics compared with the chemical physics involved in these problems. The airflow examples were chosen because flight requirements have stimulated intensive efforts toward a firm grasp of the coupled rate processes. The air system is, perhaps,

unique in this respect. Many other technically significant problems relating to propulsion and to flight in other atmospheres have motivated further detailed studies of reaction kinetics in hypersonic flows. Both the fluid dynamicist and the chemical physicist are thus confronted with further vast areas of unexplored territory.

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RESONANT CHARGE EXCHANGE IN ATOMIC COLLISIONS*

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I. INTRODUCTION

The recent study of charge exchange in atomic collisions has given us an example of wave mechanics so beautiful that it belongs to every textbook on the subject. *Resonant* charge exchange occurs in collisions between an ion A^+ and neutral atom B, where the atoms A and B have the same ionization potential. Everhart and his co-workers have recently observed such striking experimental results that theoretical investigation has been given a giant push. Although, in principle, the formalism of Massey and Smith[1] contained the laws of resonant charge exchange, our grasp was limited so that we were unable to work out the details of the simplest atomic processes without the guide of experimental results. Even the elementary process of a collision between a proton and a hydrogen atom had surprises for many of us.

In the case of the relatively simple collision He–He^+, the results were not understood by anyone until we discarded assumptions which had been held for thirty years, since Massey and Smith's paper.[1]

II. CLASSICAL RESONANCE

In the most general case of classical resonance, we can consider an oscillating system of total energy U. If damping is linear, $U = U_0 e^{-t/T}$, where T is the decay time of the total energy of oscillation. The quality factor, Q, of a system is a measure of the sharpness of the resonance:

$$Q = \omega T,$$

* This paper was presented at the La Jolla Summer School on Chemical Physics, August 1965, University of California, San Diego, California, U.S.A.

where ω is the angular frequency of oscillation. A high-Q system has many oscillations during its decay. A low-Q system is heavily damped and has few oscillations before decay.

When two oscillators are in resonance and are coupled, two *steady state* oscillations result with angular frequencies ω_s and ω_a. These correspond, respectively, to a symmetric and an antisymmetric superposition of the individual oscillations. If one oscillator alone is started, the energy is transferred back and forth with a beat angular frequency ω_B, which is a measure of the strength of the coupling:

$$\omega_B = |\omega_s - \omega_a|.$$

III. QUANTAL RESONANCE AND CHARGE EXCHANGE[2]

Heisenberg's application of the concept of resonance to quantum mechanics has a textbook example in the H_2^+ molecule. For a proton A and a hydrogen atom B at a fixed separation R, the stationary-state wave functions for the single electron become the symmetric and the antisymmetric molecular orbitals (MO):

$$1s\sigma_g = 1\sigma_g = \frac{1s_A + 1s_B}{\sqrt{2}},$$

$$2p\sigma_u = 1\sigma_u = \frac{1s_A - 1s_B}{\sqrt{2}}.$$

The eigenvalues, ε_g and ε_u, are shown in Fig. 1. If an electron is initially placed entirely on center A (initial wave function $1s_A$), it will hop back and forth from A to B with angular frequency $\omega = \varepsilon_u - \varepsilon_g$ in atomic units (a.u.).

Atomic units are used throughout this paper as follows:

1 a.u. of energy $= \mu e^4/\hbar^2 = 2E_H = 27.2$ ev.

1 a.u. of length $= a_0 = \hbar^2/\mu e^2 = 0.53$ Å.

1 a.u. of velocity $= e^2/\hbar = 2.18 \times 10^8$ cm/sec.

1 a.u. of time $= \hbar^3/\mu e^4 = 2.42 \times 10^{-17}$ sec.

It is useful to note that the energy of an ion in atomic units is given by the relation

$$E \text{ (keV)} = 25\, MV^2,$$

where M is the atomic weight and V the velocity in a.u. In atomic units, the Bohr frequency relation is simply $E = \omega$.

Formally, we can express the initial wave function of electron on atom B:

$$\Psi_{\text{init}} = 1s_{\text{B}} = \frac{1\sigma_{\text{g}} - 1\sigma_{\text{u}}}{\sqrt{2}}$$

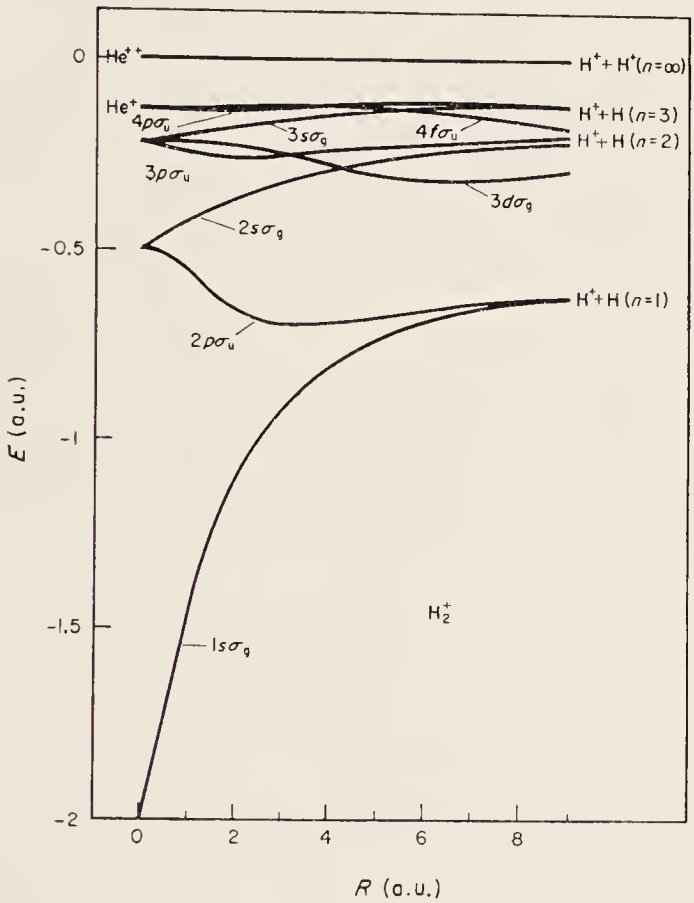

Fig. 1.

In the Heisenberg representation, the wave function is:

$$\begin{aligned}\Psi &= [1\sigma_{\text{g}} \exp(-i\varepsilon_{\text{g}}t) - 1\sigma_{\text{u}} \exp(-i\varepsilon_{\text{u}}t)]/\sqrt{2} \\ &= \frac{1s_{\text{A}}}{2}[\exp(-i\varepsilon_{\text{g}}t) - \exp(-i\varepsilon_{\text{u}}t)] \\ &\quad + \frac{1s_{\text{B}}}{2}[\exp(-i\varepsilon_{\text{g}}t) + \exp(-i\varepsilon_{\text{u}}t)].\end{aligned}$$

The squares of the coefficients of $1s_A$ and $1s_B$ give the probabilities for the electron to be on center A or B, respectively:

$$P_A = \sin^2 \tfrac{1}{2}([\varepsilon_u - \varepsilon_g]t) \tag{2}$$

and

$$P_B = \cos^2 \tfrac{1}{2}([\varepsilon_u - \varepsilon_g]t),$$

which are just the equations for the well-known quantal resonant exchange.

IV. EFFECT OF NUCLEAR MOTION

So far, in this paper, we have not been realistic, as we have taken the nuclei to be clamped at a separation R. We should examine the actual experimental arrangement. The form of the wave function depends on the process of measurement.

In most experiments of interest, the differential cross-section for charge exchange is observed. The most striking results occur at higher energy and large angles of deflection. In classical orbit theory, these collisions have impact parameters and distance of closest approach to the nuclei which are small compared with atomic dimensions. For fixed scattering angle, probability of the electron capture, plotted against reciprocal ion velocity, shows oscillations that are similar to the simple picture of charge exchange just discussed (see Fig. 2).

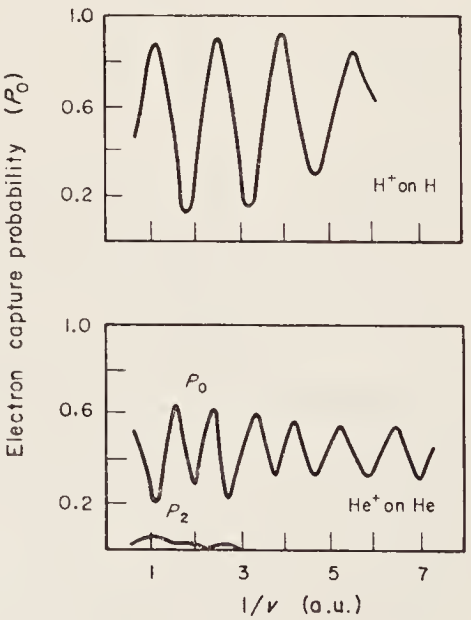

Fig. 2.

A simple impact parameter treatment, in which we treat the nuclear motion classically, reveals why. For simplicity, let the kinetic energy of the ion be large compared with the nuclear electrostatic repulsion potential. Then the velocity is a constant v, we can set the internuclear distance $R = vt$, and the arguments of expression (2) are simplified. We make the adiabatic replacement:

$$(\varepsilon_u - \varepsilon_g)t \rightarrow \int [\varepsilon_u(t) - \varepsilon_g(t)]dt = \int [\varepsilon_u(R) - \varepsilon_g(R)] \frac{dR}{v}.$$

For convenience, we call the integral

$$\int_{-\infty}^{+\infty} (\varepsilon_u - \varepsilon_g)dR = \langle Ea \rangle.$$

Then, we have for (2):

$$P_A = \sin^2 \frac{\langle Ea \rangle}{2v}$$

and

$$P_B = \cos^2 \frac{\langle Ea \rangle}{2v}.$$

For the H_2^+ molecule, the curves in Fig. 1 give $\langle Ea \rangle = 4.88$ a.u., which is in good agreement with the experimental value of (4.45 ± 0.08).

A few incidental remarks should be made about possible improvements on this simplified impact parameter treatment. First, the calculated frequency is slightly in disagreement with experiment. Also, there are phase shifts and damping which only a very detailed calculation could reproduce. We note briefly that some progress has been made in such calculations for simple systems as H_2^+ or $(He)_2^+$.[3] These calculations take into account the wave nature of the nuclear motion. In the wave treatment, we consider two wave packets of the scattered nucleus. Each packet corresponds to one of the two electronic states of the system. At high energies, the two packets follow the same quasi-classical trajectory, overlap is good, there is good interference, and oscillatory charge exchange is strong. At lower energies, the packets follow different paths and overlap is poor. Thus interference is

destroyed, and damping occurs within the two-state approximation. For total cross sections, the wave and the impact parameter treatment agree since, in the integration over all angles, the interference terms cancel. We note also that interference terms result from nuclear identity. In addition, we should include the effects of higher states and, ultimately, solve the entire problem without the approximation of using stationary states of the system at all.

Rather than consider all these details, let us focus our attention on one aspect of the problem, namely, the states and energy levels to be used in the theory of atomic collisions. Consider the specific example of the $He + He^+$ system, and use our simple impact parameter model, with its classically well-defined trajectory.

As we have said earlier, the two lowest MO's are $1\sigma_g$ and $1\sigma_u$. In the H_2^+ molecule, we found that the ground state had one electron in the $1\sigma_g$ orbital. In H_2, two electrons doubly occupy this MO. In the (unstable) $(He)_2$ molecule, we fill both MO's with four electrons; $(He)_2$ has the closed-shell electron configuration $(1\sigma_g)^2(1\sigma_u)^2$. In the He–$He^+$ collision, we have three electrons, or a single "hole" in the closed shells of the $(He)_2$ molecule. Thus the initial state of the system has the hole on the incident center A; the wave function is

$$\Psi_{\text{init}} = \frac{(1\sigma_g)^{-1} + (1\sigma_u)^{-1}}{\sqrt{2}},$$

or, more rigorously,

$$\Psi_{\text{init}} = \frac{(1\sigma_g)^2(1\sigma_u) + (1\sigma_g)(1\sigma_u)^2}{\sqrt{2}}.$$

Thus we again have a 1 : 1 mixture of two states, one with even and one with odd parity (see Fig. 3).

What happens to this mixture during the collision? The odd one, $(1\sigma_g)^2(1\sigma_u)$, goes smoothly down to the united atom limit at $R = 0$ of $Be^+(1s)^2(2p)$. The even state is crossed at $R \approx 2$ a.u. by a curve which leads to $He^+(1s)$ and an excited state of the atom, $He^* = He(1s)(2s)$. Which turn should it take at the crossing? At low velocities ($v \ll 0.1$ a.u., K.E. $\ll 1$ keV) the system avoids the crossing and takes the adiabatic path, and the even state

follows the curve $(1\sigma_g)^2(2\sigma_g)$, which lies very close to the odd state. Thus $\langle Ea \rangle$, the area between the two curves, is small and little resonant charge exchange occurs. At high energies ($v \gg 0.1$ a.u., K.E. $\gg 1$ keV) the system makes the crossing, takes the *diabatic* path, and keeps on the curve with the same MO configuration $(1\sigma_g)(1\sigma_u)^2$ with the united atom limit $Be^+(1s)(2p)^2$.

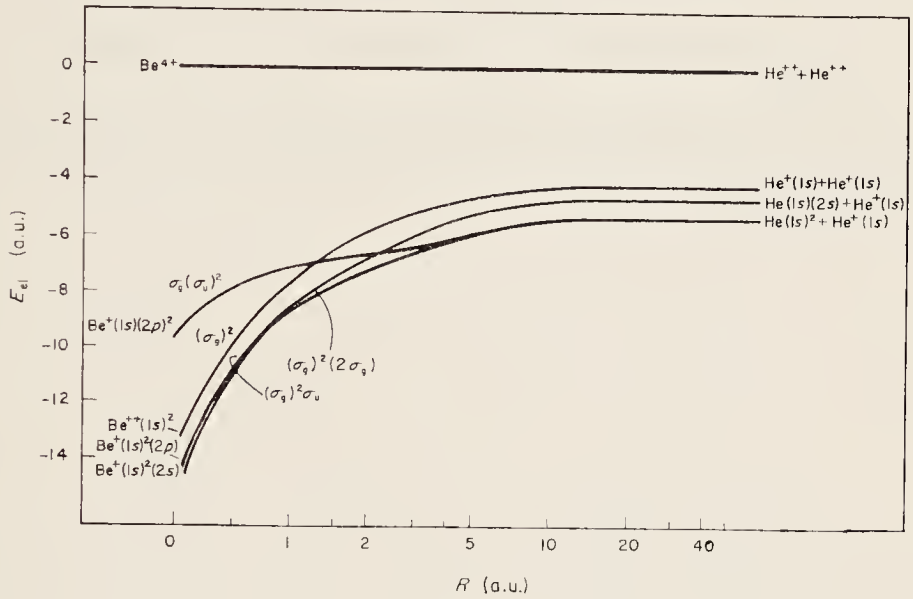

Fig. 3.

It is interesting that an infinite number of such crossings is made each time in fast collisions. It also should be noted that the $(1\sigma_g)(1\sigma_u)^2$ state is virtual. Since it lies above the doubly ionized $(He)_2^{++}$ curve, it is energetically favorable for autoionization [dropping down to $(He)_2^{++}$ plus a free electron to carry off the excess energy]. The plotting out of the form of this virtual curve is nevertheless a straightforward matter according to MO theory. The agreement between theory and experiment is as good as in the case of $H + H^+$, where the curves are known exactly.[2,3,4] This is evidence in favor of the correctness of using virtual, diabatic states in fast atomic collision theory.

At intermediate energies ($v \approx 0.1$ a.u.) neither the diabatic nor the adiabatic curve is followed. Instead, there is a good probability that in the end the system will be an excited state of the atom or

ion. Since the diabatic curve crosses a potential curve from every singly excited state of the atom or ion, a very rich set of phenomena arises in the intermediate velocity region. Excitation of metastable states of the atoms or ions or excitation of radiating states occurs strongly. We shall later give another example of these inelastic collisions.

V. QUASI-RESONANT CHARGE EXCHANGE: DAMPING[5]

The collisions of protons on helium or He^+ on H bring in some new features not present in resonant collisions. Most noteworthy is the resemblance of the charge exchange probability curve to a damped oscillation (see Fig. 4).

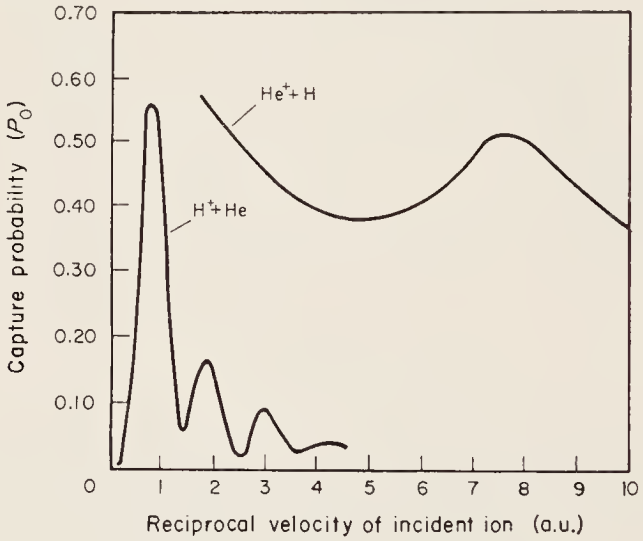

Fig. 4.

To understand this, let us follow a collision between a proton and a helium atom. Initially both electrons are in the lowest MO, $(1\sigma)^2$, which is the same as $He(1s)^2$ in the separated atoms (see Fig. 5). If the collision is sufficiently slow, both electrons will stay in the (1σ) MO and therefore will stay on the helium atom after the collision. If the collision is fast enough, one electron can jump to the (2σ) MO, the system separates as $(He^+ + H)$, and charge exchange has taken place. (Fig. 5 shows diabatic electronic

energy curves. These curves differ only slightly in energy at very small R from adiabatic curves for this system.) At just what speed this transition takes place, we cannot say without extremely detailed calculations, which have not been done completely satisfactorily yet for this simple two-electron system.

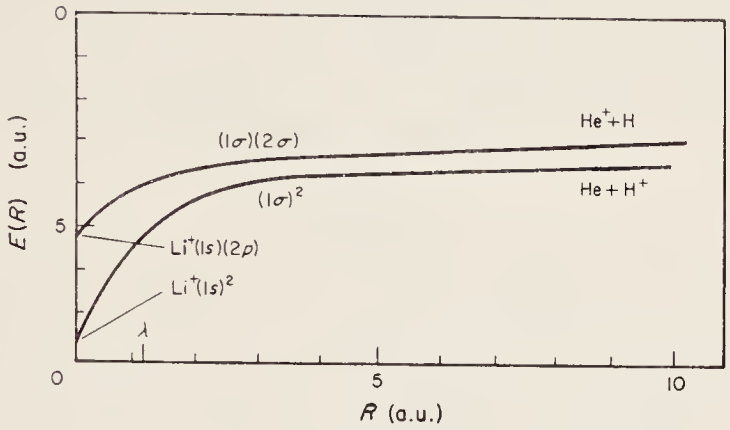

Fig. 5.

Let us look at a model which seems to help us understand this process. For very large R, the system consists of two separated atoms which do not interact strongly. For $R \ll \lambda$, a characteristic distance we call the *effective range*, the nuclei are so close together that the system resembles the "united atom." [We call the energy splitting between the two states in the united atom $R(0)$.] It should be noted that at $R = 0$, $1s\sigma$ and $2p\sigma$ have strictly even and odd parities. In the united atom, the diabatic MO's show no evidence that the charge exchange was non-resonant in the separated atoms. For $R \approx \lambda$, the system makes the transition from separated atoms to the united atom. Presumably it is during the time that the system goes through this molecular region ($R \approx \lambda$) that the electronic wave function rearranges most violently and transitions among MO's are most likely to occur.

We now have a picture for charge exchange in the case of sudden collisions. As the colliding nuclei quickly pass $R \approx \lambda$, the electrons do not have time to rearrange. They possess a 1 : 1 mixture of ground- and excited-state wave functions, just as in the resonant case. The amount of charge exchange in this situation

will depend on the area between these curves, just as before, except that the integration must be cut off at $R \approx \lambda$, in order that we count only the effective interaction region.

Now we can ask when such a quasi-resonant charge exchange can occur. For a sudden transition to occur, the splitting $E(\infty)$ between $He–H^+$ and $H–He^+$ is small compared with the uncertainty width during the collision time T, $E(\infty) \ll 1/T$. But for many oscillations to occur during the collision $\omega T \gg 1$; or setting $\omega \approx E(0)$, we have $E(0)T \gg 1$. Combining these two relations, we have a condition for resonant charge exchange:

$$Q = \frac{E(0)}{E(\infty)} \gg 1.$$

In analogy with classical resonance, we define a factor Q as a measure of the quality of the resonance. The $H^+ + He$ data in Fig. 4 are for a system with $Q = 6.7$. Even in a purely resonant charge exchange, the various causes of damping seem to keep the effective Q from being much larger than 10. For $Q \lesssim 3$, there is practically no trace of oscillatory charge exchange. Thus we have a convenient parameter for classifying atomic collisions:

Q	Classification
0–3	Non-resonant
3–10	Quasi-resonant
>10	Essentially resonant

(A brief remark is required about the lack of symmetry between $He–H^+$ and $H–He^+$ collisions. The reason for this is a matter of statistics. All $He–H^+$ collisions are in a singlet state of the electronic spin, whereas three-quarters of $H–He^+$ collisions are in low-Q triplet collisions.)[5]

Recently Perel *et al.*[6] have observed charge exchange in collisions between slow alkali ions and atoms. Fig. 6 shows the charge-exchange cross section for $Cs–Rb^+$, which evidently is rather high-Q. This is in reasonable since $E(\infty)$ for this system is only a fraction of an eV. The oscillations should be much more pro-

nounced if differential, rather than total, cross-sections were observed. Since the alkali-metal ion is a tightly bound core, these collisions may involve a simple one-electron type of charge exchange, which is analogous to proton–hydrogen collisions.

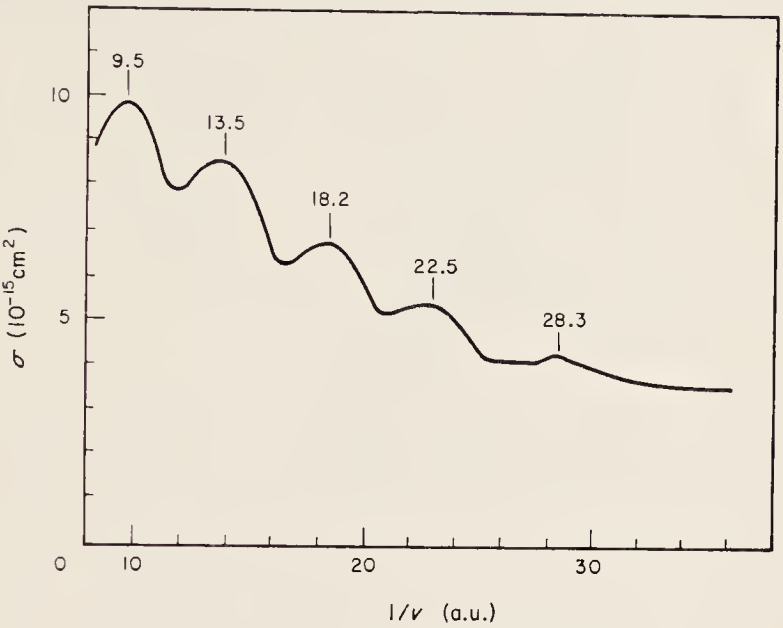

Fig. 6.

Several other relatively elementary systems can be expected to show resonant, or quasi-resonant, charge exchange.[5]

VI. MULTIPLE IONIZATION

Ar–Ar^+ collisions at ~50 KeV occur just in the velocity range where inelastic transitions between MO's are expected at crossings. Experimentally, small impact parameter collisions near this energy produce a most remarkable ionization.[7,8] As many as ten electrons can spray forth from a single collision. These electron showers are associated with characteristic energy losses in the range 0–50 eV plus integral multiples of a "quantum" of energy of about 200 eV. Furthermore, these losses seem to occur at particular internuclear separations. Fig. 7 shows the energy loss in Ar–Ar^+ collisions as a function of the distance of closest approach.

The cause of these odd phenomena has been a source of conjecture for some time. A straightforward interpretation can be made with MO theory.[9] Two colliding multi-electron atoms have far too complex a system of energy curves of states of the whole

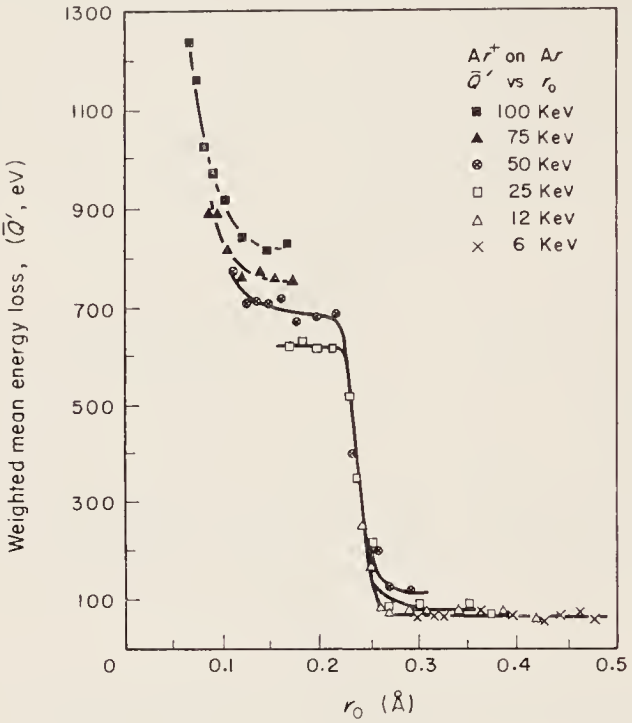

Fig. 7.

system. Instead, we examine the curves of the individual electrons, i.e. molecular-orbital energy-level diagrams. Fig. 8 shows such a diagram for the $(Ar)_2$ system, with diabatic correlation for MO's between separated and united atom limits. It should be noted in particular that the $4f\sigma$ MO is "promoted" from an inner shell of the argon atom to an outer shell. If the $4f\sigma$ electron takes a wrong turn at any of a large number of crossings, it can remain in an outer shell after the collision. Such wrong turns are statistically very probable in the right energy range for small enough impact parameters. The result is an atom or ion with an inner-shell "hole."

Such excited atomic states have been known experimentally and studied theoretically for many years in the fields of X- and

β-ray spectroscopy. It is known that these states are autoionizing and end with multiple electron emission.

The simple picture presented here agrees well with experiment in the prediction of (1) characteristic energy losses, (2) critical internuclear distances for increase of energy loss, and (3) the

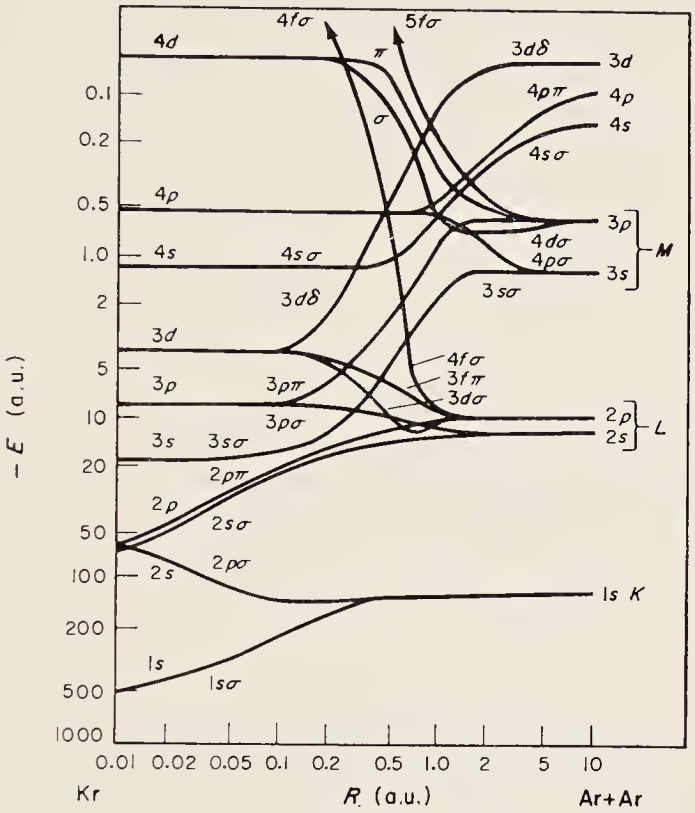

Fig. 8.

number of ejected electrons. In addition, we expect the energy distribution of ejected electrons to have strong peaks near the "quantum" of 200 eV. Search for these peaks is crucial to distinguish between the MO and other interpretations of the experiments.

Finally, it should be pointed out that the MO energies given in Fig. 8 represent only the crudest guesses. These should be calculated rigorously. Molecular-computation experts have fixed their attention on the difficult problem of calculating chemical

binding energies, which are but a fraction of an atomic unit. The chemical bond's perturbation of the MO energy levels would hardly be visible on Fig. 8. Only the most detailed and refined calculations can be expected to give the subtle changes in the electronic wave functions concerned with chemical bonds.

In fast atomic collisions, we have seen the interesting effects come from massive shifts of MO energies (see Figs. 1, 3, and 8) of several atomic units. Calculation of these gross effects would represent but a small fraction of the effort that has been spent to date on MO computations. The rate of return of investment in this area seems high and makes worthwhile the study of atomic collision problems by the adventurous molecular theorist.

The author is indebted to Willis Lamb for a helpful discussion.

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ELECTRONEGATIVITY AND CHEMICAL BONDING*

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I. INTRODUCTION

This paper is essentially concerned with the question: what is the relationship between the chemical concept of electronegativity and the existing theories of molecular electronic structure? more specifically, to what extent can the concept of electronegativity be incorporated within the framework of the present approximations to the chemical bond? Before starting the analysis, however, we should ask whether such questions are valid and timely. We know that *ab initio* calculations of molecular properties leave no place for concepts such as electronegativity. About thirty

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years ago Mulliken[84] expressed the fear that the idea of electronegativity would outlive its usefulness, and there is little doubt that, if and when chemistry is reduced to a branch of applied mathematics, we shall have no need for such concepts. Nonetheless, as long as we try to understand chemistry in chemical terms, our question remains legitimate. As for the need of such undertaking at the present time: this problem was discussed some time ago by Mulliken,[85] by Moffitt,[79,81] and by Pritchard and Skinner.[109] Recently, however, new ideas on electronegativity have been proposed by Iczkowski and Margrave,[60] Klixbüll Jørgensen,[62] Hinze, Whitehead, and Jaffe,[55] and Klopman.[64] Klopman has also revived the problem of the relation between electronegativity and the diagonal matrix elements of the LCAO–MO approximations,* already discussed by Coulson and Longuet–Higgins,[25] Moffitt,[79] Mulliken,[85] Laforgue,[66] Pearson,[101] Chalvet and Daudel,[20] Parr and Pariser,[91] Pritchard and Sumner,[110] and more recently by Barnum,[7] Julg,[61] and Berthier, Millie, and Veillard.[14] This problem is becoming serious because of the increasing number of semi-empirical calculations of many systems,[6,7,10,11,13,14,22,38,39,42,46,57,58,61,74,78,88,107,110a,125,128] and the uncertainties besetting the off-diagonal elements.† Also, electronegativity differences have always been connected with bond polarity, and it is increasingly recognized that this property is a function not only of atomic terms but also of molecular terms.[41,64] Thus, it seems that a discussion of these problems is needed at the present moment. This paper deals mainly with the relations between electronegativity, molecular-orbital theory, and valence-bond theory, and it is not an exhaustive review of the concept of electronegativity and its applications to chemical problems. A

* In the very first MO treatment of heterocyclic compounds by G. W. Wheland and L. Pauling [*J. Am. Chem. Soc.*, **57**, 2086 (1935)] the value given to the difference $\alpha_N - \alpha_C$ shows that the diagonal elements are being identified with the electronegativities.

† The Wolfsberg–Helmholz approximation,[134] although still useful, suffers from the fact that the numerical results are strongly dependent of the value of the constant K.[22,39,107] An analysis of the increasingly available number of computed off-diagonal elements[87] will perhaps provide us with better approximate formulae. A careful analysis of the SCF Hamiltonian of the off-diagonal matrix elements is being carried out by Mr. Harold Basch (Columbia University).

worthy continuation of Pritchard and Skinner's invaluable review is still to come.[109]

Chemists have an intuitive feeling for what is meant by electronegativity of an atom and, in fact, this concept goes back to Berzelius[15] who first published what amounts to a scale of electronegativity around 1830. During the following seventy years, with the falling in disfavor of the dualistic theory and the great progress of the structural theory of organic chemistry, problems connected with the electrostatic nature of the chemical forces and the polarity of bonds were not in the forefront of chemical thought. Around the turn of the century, with the discovery of the electron, a revival of interest in this problem took place, becoming associated the names of Abegg, Bodländer, Thomson, Falk, Nelson, and Fry. This phase culminated in the great works of Lewis[69] and of Kossel.[65] During the twenties the arrival of quantum mechanics finally furnished the tools for an understanding of the chemical bond. The problem of the ionic character of bonds was analyzed from the viewpoint of wave mechanics,[94] and a scale of relative electronegativities was established,[95] electronegativity being defined[97] as "the power of an atom in a molecule to attract electrons to itself."

This broad definition is unavoidably vague (we do not know precisely what is meant by "power," or which electrons are being referred to) but the qualification "an atom in a molecule" is significant. It emphasizes that chemists are interested in the attraction of bonding electrons by atoms as they are in the molecules and in its connection with bond polarities, bond energies, etc. But if we define electronegativity as a function of molecular parameters, or, more correctly, as a function of molecular noninvariants—the coefficients in a LCAO–MO or VB wave function for the molecule—then strictly speaking it is meaningless to consider electronegativity as an atomic parameter. Because molecules are not just simple additive combinations of atoms[86] *it is impossible, in principle,* to assign to each atom a definite electronegativity.[85,122a] Recourse to a definition of orbital electronegativity[55,81–85,109,130] does not solve the difficulty. Electronegativity is definitely not an atomic parameter, as are the ionization potential and the electron-affinity, nor is it an atomic orbital parameter, as are the valence-state ionization

potential,[82,127] the valence-orbital ionization potential,[10] the orbital radius,[129] etc. This is a fundamental difficulty, repeatedly pointed out by Mulliken[83–86] and recently discussed in a series of papers by Spiridonov and Tatevski.[122a] However, the admittedly approximate theories of the chemical bond, the LCAO–MO methods, and the VB methods, in a way "preserve" the atoms in the molecules, and it is with the relations between these approximations and electronegativity that we are mainly concerned. Also, the usefulness of what I have called "zeroth-order approximations" makes the knowledge of atomic electronegativities significant for the rationalization of chemical phenomena at this level.*

II. ELECTRONEGATIVITY AND VALENCE BOND THEORY

1. Mulliken Scale

The modern concept of electronegativity arose from general considerations based in the VB method.[82,95] In the perfect-pairing approximation of the VB method the wave function of a diatomic molecule AB is:

$$\Psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3, \qquad (1)$$

where $\phi_2 = \sqrt{\frac{1}{2}}[\chi_A(1)\chi_B(2) + \chi_A(2)\chi_B(1)]$, $\phi_1 = \chi_A(1)\chi_A(2)$, $\phi_3 = \chi_B(1)\chi_B(2)$, and χ_A and χ_B are the valence orbitals of atoms A and B, and the c's are constants. Each function is multiplied by the same spin factor. ϕ_1, ϕ_2, and ϕ_3 do not necessarily form an orthogonal set† but this fact does not invalidate equation (1)

* Zeroth-order approximations to chemical bonding are those in which molecular properties are obtained from atomic parameters.[41] The much used expression "semiempirical approximations" is objectionable since even the so-called *ab initio* calculations are semiempirical in the sense that the mass and the charge of the electron, and the Planck constant, are not normalized from theory but are obtained from experiment. We can only speak of different levels of empiricism, and for the chemist the zeroth level is the one that starts from the unperturbed atomic terms.

† For example,[17] in the case of the molecule H_2 the covalent function of Wang and Weinbaum's ionic terms have an overlap of 0.95. The non-orthogonality of ϕ_1, ϕ_2, and ϕ_3 means that the squares of the coefficients in eqn. (1) do not give the expectation values of the eigenvalues of any operator (in particular, for the Hamiltonian operator they do not give the expectation values of the energies).

since the variation method does not require orthogonality of the terms of the linear combination. ϕ_1 is generally considered as the eigenfunction of the system A^-B^+, and similarly for ϕ_2 and ϕ_3. However, if the eigenvalues of these functions are the differences in energy between the systems A^-B^+, A–B, A^+B^-, and the separated atoms (that is, the bond energies), then ϕ_1, ϕ_2 and ϕ_3 must be considered as the wavefunctions of the bonding electron pair, or, alternatively, they represent the three possible electron-pairing schemes for the system. They are, in fact, antisymmetrized two-electron wave functions in the field of the core A^+B^+ and, following Shull,[2,119] we shall call them "geminals."

The electronegatives of atoms A and B are said to be equal, $X_A = X_B$, if $c_1 = c_3$. If

$$H_{12} = \int \phi_1^* \mathfrak{H} \phi_2 d\tau = H_{23} = \int \phi_2^* \mathfrak{H} \phi_3 d\tau,$$

the equality $c_1 = c_3$ implies* that $H_{11} = H_{33}$. But the integral $H_{11} = \int \phi_1^* \mathfrak{H} \phi_1 d\tau$ is, up to a constant, the energy of the geminal ϕ_1 and $H_{33} = \int \phi_3^* \mathfrak{H} \phi_3 d\tau$ is (up to the same constant) the energy of

* The secular equations for the wave function (1):

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) + c_3(H_{13} - ES_{13}) = 0$$
$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) + c_3(H_{23} - ES_{23}) = 0$$
$$c_1(H_{31} - ES_{31}) + c_2(H_{32} - ES_{32}) + c_3(H_{33} - ES_{33}) = 0$$

By taking co-factors and crossing out the second row in each case, one gets:

$$\frac{c_1}{c_3} = \frac{\begin{vmatrix} H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{32} - ES_{32} & H_{33} - ES_{33} \end{vmatrix}}{\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{31} - ES_{31} & H_{32} - ES_{32} \end{vmatrix}}$$

If $c_1/c_3 = 1$, one has further:

$$(H_{12} - ES_{12})(H_{33} - ES_{33}) - (H_{13} - ES_{13})(H_{32} - ES_{32}) = (H_{11} - ES_{11})(H_{32} - ES_{32}) - (H_{12} - ES_{12})(H_{31} - ES_{31}).$$

Since the Hamiltonian is Hermitean, it follows that $H_{11} = H_{33}$ if $H_{12} = H_{23}$ and $S_{12} = S_{23}$. I am indebted to Dr. Peter Politzer with regard to this point.

the geminal ϕ_3, the Hamiltonian being the core Hamiltonian. These integrals can be partioned in the following way:

$$H_{11} = \int \phi_1^* \mathfrak{H}_A \phi_1 d\tau + \int \phi_1^* \frac{e^2}{r_{B_1}} \phi_1 d\tau, \tag{2}$$

$$H_{33} = \int \phi_3^* \mathfrak{H}_B \phi_3 d\tau + \int \phi_3^* \frac{e^2}{r_{A_3}} \phi_3 d\tau, \tag{3}$$

where $\mathfrak{H}_A$ and $\mathfrak{H}_B$ are the atomic Hamiltonians and r_{B_1} and r_{A_3} are the co-ordinates of the geminals ϕ_1 and ϕ_3 with respect to the cores B^+ and A^+, respectively. If the reasonable supposition is made that, for *rigid cores*, $\int \phi_1^* \frac{e^2}{r_{B_1}} \phi_1 d\tau = \int \phi_3^* \frac{e^2}{r_{A_3}} \phi_3 d\tau$, then the condition of equal coefficients c_1 and c_3 corresponds to

$$\int \phi_1^* \mathfrak{H}_A \phi_1 d\tau = \int \phi_3^* \mathfrak{H}_B \phi_3 d\tau.$$

But $\varepsilon_A = \int \phi_1^* \mathfrak{H}_A \phi_1 d\tau$ is the energy of the geminal ϕ_1 centered in A, and $\varepsilon_B = \int \phi_3^* \mathfrak{H}_B \phi_3 d\tau$ is the energy of the geminal ϕ_3 centered in B. Now, the energy of the geminal ϕ_1 centered in A is equal to the energy of the atomic orbital χ_A with occupation number 2, and this is given by the sum of the valence-state ionization potential and the valence-state electron-affinity, $\varepsilon_A = -(\mathrm{VSIP} + \mathrm{VSEA})_A$. Similarly we can write $\varepsilon_B = -(\mathrm{VSIP} + \mathrm{VSEA})_B$. Hence the sum of the VSIP and the VSEA of an atom is a measure of the electronegativity of this atom.[82] It is convenient to express the electronegativities as positive numbers and to consider the energy *per electron*, arriving to Mulliken's definition of electronegativity, $X_A = 1/2(\mathrm{VSIP} + \mathrm{VSEA})_A$, $X_B = 1/2(\mathrm{VSIP} + \mathrm{VSEA})_B$.

A more rigorous presentation of these arguments was outlined by Moffitt[80] who found that the condition $c_1 = c_3$ in the VB function is obeyed, for all values of the interatomic distance, if, and only if $\varepsilon_A - \frac{1}{2}J_{AA} = \varepsilon_B - \frac{1}{2}J_{BB}$, where ε_A and ε_B are the Hartree-Fock energies of the atoms and J_{AA} and J_{BB} are the inter-electronic Coulomb integrals. If one writes $\varepsilon_A = I_A$ and $\varepsilon_B = I_B$, and if the approximation[79,90] $J_{XY} = (I_Y - A_Y)$ is used, then $c_1 = c_3$ corresponds to $\frac{1}{2}(I_A + A_A) = \frac{1}{2}(I_B + A_B)$, where I_A and I_B are the VSIP's and similarly A_A and A_B are the VSEA's. Mulliken's definition of electronegativity is again obtained.

Valence-state ionization potentials and electron affinities of many elements in divers valence states are now available in the literature,[10,21,54,64,81,104,109,121,122] and this initial limitation in the general use of Mulliken's values is no longer valid.

2. Pauling Scale

The Pauling electronegativity scale[97] has had a great success in correlating chemical phenomena. The general VB arguments behind it are as follows: if $(I_A + A_A) \gg (I_B + A_B)$, equation (1) reduces to:

$$\Psi = c_1\phi_1 + c_2\phi_2, \tag{4}$$

where ϕ_1 represents the ionic structure A^-B^+ and ϕ_2 the covalent structure A–B.* Application of the variation method leads to the secular equations:

$$\begin{aligned} c_1(H_{11} - E) + c_2(H_{12} - ES_{12}) &= 0; \\ c(H_{21} - ES_{21}) + c_2(H_{22} - E) &= 0. \end{aligned} \tag{5}$$

If, as generally assumed, $H_{11} = \int\phi_1^*\mathfrak{H}\phi_1 d\tau$ is the ionic bond energy and $H_{22} = \int\phi_2^*\mathfrak{H}\phi_2 d\tau$ is the normal covalent bond energy, the lower root of (5) is the bond energy† of AB:

$$E_{AB} = \frac{[(H_{11} + H_{22}) - 2H_{12}S_{12}] + \sqrt{(H_{11} - H_{22})^2 + 4\,(H_{11}S_{12} - H_{12})(H_{22}S_{12} - H_{12})}}{2(1 - S_{12}^2)} \tag{6}$$

Equation (6) shows that the bond energy is a function of polycenter integrals (H_{11}, H_{22}, H_{12}) and that it is impossible to calculate the coefficients c_1 and c_2 from a consideration of atomic

* This simplification, however, breaks the one-to-one correspondence between the VB and the MO wave functions (see below).

† This follows K. S. Pitzer.[106] Strictly, H_{11} is the total energy of A^-B^+, H_{22} is the total energy of A–B, etc. The roots of the secular equations, however, are not affected if one subtracts a constant term (here the sum of the electronic energies of atoms A and B at infinite separation) from the diagonal elements of the determinant and if ϕ_1 and ϕ_2 are orthogonal. The last condition rarely obtains in actual VB calculations.

terms only. H_{11} is generally approximated by an expression of the type[16]

$$\left\{\frac{e^2}{r} - Be^{-kr} + A_A - I_B\right\},$$

or some other potential function (the Born–Mayer potential as written is positive for any reasonable value of r; hence the bond energy E_{AB} is also positive). H_{22}, the normal covalent bond energy,* is approximated by the arithmetic-mean or the geometric-mean rule.[93,96] If momentarily we leave aside the many doubts about the validity of such rules, no simple relation between the bond energy E_{AB} and the normal covalent bond energy is to be expected. Pauling, however, found that the following equation gives reasonable results for single bonds that are not highly ionic:

$$E_{AB} = H_{22} + (X_A - X_B)^2; \tag{7}$$

here, X_A and X_B are atomic parameters which were identified by Pauling with the electronegativities, that is, the electron-attracting powers of atoms A and B. Since only the differences $X_A - X_B = \sqrt{E_{AB} - H_{22}}$ can be known, X_A and X_B are *relative electronegativities*. Remarkably, Pauling's values are proportional to Mulliken's electronegativities[109] and thus can be rendered absolute.†

Rationalizations of equation (7) in terms of the MO description will be described below. Presently we shall be content with the question: what is the VB basis for equation (7), hence for Pauling electronegativity scale?

Substitution of the wavefunction (4) into the wave equation $\mathfrak{H}\Psi = E\Psi$ gives:

$$E_{AB} = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}}{c_1^2 + c_2^2 + 2c_1 c_2 S_{12}}. \tag{8}$$

* The normal covalent bond energy as originally defined by Pauling and Yost[93] does not correspond to the Heitler–London function ϕ_2 but to a Weinbaum function $\phi' = c_1'\phi_2 + c_2'(\phi_1 + \phi_3)$. For this reason the quantity $\Delta = E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})$ is called the "excess ionic resonance energy." Since the coefficient c_2' of the ionic structures in Weinbaum's function is very small, the error is negligible.

† The two scales, however, differ in their units. Mulliken's values are in energy units (eV) or in units of potential (energy per electron). Pauling's numbers are in one-half power of energy [$(eV)^{\frac{1}{2}}$].

Now, equation (7) furnishes reasonable results only if the bonds are not extremely polar.* Hence, making $c_1^2 = 0$ and $2c_1c_2S_{12} = 0$, equation (8) transforms into:

$$E_{AB} = H_{22} + 2c_1/c_2H_{12}. \tag{9}$$

Comparing (7) with (9) shows that the Pauling scale is based on a direct proportionality between $(c_1/c_2)H_{12}$ and the square of the difference of two atomic parameters. As can be seen from equation (8) the covalent contribution to the actual bond energy is the product of the normal covalent bond energy multiplied by the weight of the covalent wave function, $c_2^2H_{22}$. On simplification to (9), H_{22} appears with a coefficient of 1 and is overvalued, the more so in the very ionic cases. On the other hand, the energy of the ionic structure, H_{11}, is dropped. That the numerical values of Pauling electronegativities are (roughly) proportional to Mulliken's absolute electronegativities is probably the result of a remarkable cancellation of errors. In historical perspective this fact vindicates Pauling's genial intuition. One feels, however, that Burawoy's criticism[18] cannot be lightly dismissed and that equation (7) has no quantum-mechanical basis. In particular, equation (7) fails in the case of the alkali-metal hydrides, for which $E_{AB} < \frac{1}{2}(E_{AA} + E_{BB})$. The geometric-mean rule eases the failure somewhat, and still better results are found with the reciprocal-mean rule,[1] but none of these rules has a sound theoretical basis.

Because of the easy accessibility of thermochemical data and its fair success in predicting single-bond energies, Pauling electronegativities have been used as a gauging scale† by many authors[3,4,23,29,48,50,67,70,73,77,115,116,124,131] who established electronegativity scales based on various atomic and molecular properties. It is interesting, therefore, to discuss some further approximations involved in deriving the Pauling scale.

* Pauling[98] states that the calculated E_{AB} is too high if $(X_A - X_B) > 1.5$. Analysis of "thermochemical" electronegativities are found in Huggins,[59] Fineman and Daignault,[44] and Allred.[5]

† Allred,[3,4] Sanderson,[116] and Lakatos[67] argue for a scale not entirely comparable with Pauling's in that $X_{Ge} > X_{Si}$, $X_{As} > X_P$, and $X_{Se} > X_S$. Because of the neglect of molecular-energy terms (see below) the alternation in electronegativities may be not as marked as supposed by these authors. For a recent analysis of the evidence for alternation in the electronegativities of Group IV elements from chemical shifts in NMR spectra,[3,4] see Drago.[36]

The validity of the arithmetic-mean rule,[93] or, alternatively of the geometric-mean rule,[96] has been questioned by, among others, Coulson.[26] Coulson pointed out that the bonding orbitals χ_A and χ_B in the molecule AB may not be exactly the bonding orbitals of atoms A and B in the homo-atomics A_2 and B_2. In other words, the hybridization state may change in going from one molecule to another. Also, the interatomic equilibrium distance in the molecule AB is not the same as the bond distance of a purely covalent bond A–B (wave function ϕ_2) supposedly given by the sum of the covalent radii; in general $r_{AB} < (r_A^{cov} + r_B^{cov})$, and the so-called bond contraction is roughly proportional to $(X_A - X_B)$.[117,132a] The bond contraction, relative to the sum of the covalent radii, may be due to an additional potential over the normal covalent-bond energy curve,[9] and the additional potential possibly is the Madelung–Jørgensen energy of the ionic contribution, H_{11}.[56] Mulliken's derivation[85] of the equation $\beta_{AB} = \frac{1}{2}(\beta_{AA} + \beta_{BB})$, where the β's are the off-diagonal elements of the secular determinant, has been considered as a justification for the arithmetic-mean rule, but his equation is based in the additivity of the overlap integrals and this is in itself an approximation. The geometric-mean rule, on the other hand, is based on considerations in which the radial parts of the orbitals χ_A and χ_B are completely neglected. With the limitations of its basic postulates in the background, let us now analyze some of the extensions of the Pauling scale.

3. Electronegativity and Ionic Character of Bonds

Malone[77] called attention to the relation between electronegativity difference and the electric dipole moment of molecules. Fajans[37] and Pauling[97] assumed that the ratio μ/er, where μ is the experimentally determined dipole moment, measures the *ionicity* of the bond in diatomics.* It is well established now that this assumption is not warranted since the total dipole moment is the sum of the primary, homopolar, and hybridization moments.[24,83]

* Fajans' paper antedates the quantum-mechanical interpretation of chemical bonding. The ratio μ/er was called by Fajans "degree of polarity." Beginning in 1920 Fajans published a number of papers in which he also anticipated the (rough) transferability property of bond-energy terms, predicted by quantum mechanics.[34]

Pauling found, however, that on the basis of the original assumption a simple relation holds between the ionicity $c_I^2 = \mu/er$ and the electronegativity difference. The relation is $c_I^2 = 1 - \exp[-a(X_A - X_B)^2]$. Expanding the exponential in a power series and neglecting higher terms, one has, for small values of $(X_A - X_B)$, $c_I^2 \approx (X_A - X_B)^2$. In any case, the conclusion is obtained that the ionicity is a unique function of the electronegativity difference. Information about the bond ionicity, i.e., about the charge asymmetry along the internuclear distance can be gleaned from a variety of physical methods such as nuclear quadrupole resonance,[30,49,111,125]; nuclear magnetic resonance,[19,31,51] etc. Electronegativities obtained from such measurements and the assumption of a one-to-one correspondence between ionicities and differences in electronegativities[3,4,29,48,50,77,131] could be called *secondary electronegativities*;[60] for we have now experimental evidence that the assumed uniqueness is not valid. Dailey and Townes[32] found that the lithium halides are more ionic than the corresponding sodium halides, even though $(X_{Hal}-X_{Na}) > (X_{Hal}-X_{Li})$. Kaufman, Wharton, and Klemperer[63] recently found that SrO(g) is more ionic than BaO(g). This behaviour is predicted by the localized-orbital MO theory[89] and also by the zeroth-order order approximations in which the ionicity is a function of atomic-term values and molecular-energy terms.[41]

Electronegativity differences have also been correlated with molecular properties other than ionicity. For example, Klixbüll Jørgensen[62] found that in metal complexes the wave number of the charge-transfer transition maximum is directly proportional to the electronegativity difference between the ligand and the central atom. His "optical electronegativities" are very close to Pauling's. Klixbüll Jørgensen notes that although these simple relations are *a priori* improbable they are usable because of fortuitous cancellations of electron-electron repulsion integrals and other polycenter integrals.

In retrospect I submit that Mulliken's definition, $X_A = \frac{1}{2}(I_A + A_A)$, is the basic definition of atomic electronegativity. It gives the variation of X as a function of the valence state (atomic-orbital hybridization), it can be rendered charge-dependent (see below), and it implies the fundamental importance of the electron-pair functions (geminals). This does not mean that his values

correlate best with molecular properties, such as bond polarity, nuclear quadrupole coupling constant, etc. Since these properties are also functions of molecular terms, other scales (secondary scales) can possibly correlate better. On the other hand, electronegativities based on other atomic parameters such as atomic potentials, $Z^{eff}e^2/r$ (ref. 48), or the force acting on a valence electron, $Z^{eff}e^2/r^2$ (refs. 3, 67), should be used only insofar as they are proportional to Mulliken's values. The very fact that two different electronegativity scales have been proposed based on differing powers of the covalent radii shows the limitations of these scales.

Pauling's electronegativities[5,97] stand apart. His numbers are proportional to Mulliken's[109] and they may represent averages over the range of valence states exhibited by different elements, and because thermochemical electronegativities are known for most elements they remain useful to the chemists. In each group of elements the range of Pauling's values tends to be wider than Mulliken's. For the halogens, for example, Pauling's numbers vary from 4.0 (F) to 2.4 (I), whereas Mulliken's, multiplied by a suitable factor, range from 3.9 to 2.5. For small electronegativity differences this is an advantage of the Pauling scale, since the ever-present Madelung–Jørgensen energy (see below) tends to increase the bond polarity. As was pointed out above, for highly polar bonds equation (7) gives too large bond energies,[99] owing to overestimation of the covalent bond energy. It should be noted that Pauling's numbers have a sort of "built in" charge correction, since they refer to the atoms as they are in the molecules. If one uses the neutral-atom electronegativities obtained by Daudel and Daudel[33] directly in equation (7) one obtains still higher (i.e., worst) results, although if the Daudels' values are used together with their iterative procedure better results are obtained.

III. ELECTRONEGATIVITY AND MOLECULAR ORBITAL THEORY

1. Electronegativity and LCAO-MO Methods

The VB method and the LCAO-MO method (including configuration interaction) are fundamentally identical. Consequently we should expect that the concept of electronegativity would fit

as easily within the framework of MO theory as it did in the VB case. Unfortunately it will be shown that this is not so, and the reason arises from the following considerations: The perfect-pairing approximation of VB methods involves two-electron wave functions. Manageable MO methods, on the other hand, involve one-electron wave functions (and one-electron Hamiltonian operators), and the electron–electron interaction can only be introduced as an average potential. This continual reference for individual electrons in molecular-orbital theory has some advantages in dealing with one-electron properties, such as ionization potentials, electronic spectra, hyperfine splitting of ESR spectra, etc. This is not true in VB methods, where, as Coulson says,[27] we are obliged to consider wave functions intimately involving two electrons. Consider now what Dewar[35] calls "collective properties": charge distribution, bond energies, equilibrium bond distances, etc. In the rigid-core approximation the collective properties are, in fact, electron-pair properties. As such they are much better dealt with by two-electron theories such as the valence-bond method. But those are precisely the properties that are related to electronegativity. The use of geminals as the true invariants in chemical bonds solves the electron–electron interaction problem (including correlation) in a natural way, whereas this problem plagues the one-electron theories and makes the relation between electronegativity and MO parameters difficult to analyze. Here we are content to discuss only the LCAO approach to molecular orbitals as applied to closed-shell systems. This is in itself an approximation that somewhat preserves the original atomic orbitals. Molecular wave functions can be constructed (for example, the James and Coolidge wave function) that are not related to the states of the free atoms. The partitioning of molecular energies in Coulomb and exchange terms is an artefact of the LCAO method, and quantities such as the Coulomb integral, etc., are not true invariants and as such no basic physical meaning can be associated with them.

2. Mulliken's Approach

Mulliken's original suggestion[82] that electronegativity is given by $X = \frac{1}{2}(I + A)$ was based on VB arguments. In 1949, in the first of two important papers on the MO theory,[85] he proposed a

justification for his scale from MO considerations.* Let $\Psi_{MO} = a\chi_A + b\chi_B$ be a bonding localized MO; if a = b we say that the bond is non-polar. From the solutions of the secular equations the condition a = b is realized if $\alpha_A = \alpha_B$, where $\alpha_A = \int \chi_A^* \mathfrak{H} \chi_A d\tau$ and $\alpha_B = \int \chi_B^* \mathfrak{H} \chi_B d\tau$ are the Coulomb integrals, the Hamiltonian being the complete molecular Hamiltonian. Mulliken proposed to consider $-\alpha_A$ as the absolute electronegativity of atom A, X_A, and similarly $X_B = -\alpha_B$. For the one-electron two-center system AB^+:

$$\begin{aligned} \alpha_A &= \varepsilon_A + \int \bar{u}_b \chi_A^* \chi_A d\tau \\ \alpha_B &= \varepsilon_B + \int \bar{u}_a \chi_B^* \chi_B d\tau \end{aligned} \tag{10}$$

where ε_A and ε_B are the atomic SCF one-electron energy eigenvalues, and $\bar{u}_b$ and $\bar{u}_a$ are the potential-energy operators for a single electron in the field of B^+ and A^+, respectively. Now, α_A contains a term that depends only on atom A, $\varepsilon_A \cong -I_A$, and a term, the core-electron attraction, that depends on both atoms of the bond; and similarly for α_B. Because the bond polarity depends on the difference $(\alpha_A - \alpha_B)$, and since the equality $\int \bar{u}_b \chi_A^* \chi_A d\tau - \int \bar{u}_a \chi_B^* \chi_B d\tau = 0$ is approximately valid, the core integrals can be dropped and we may define the absolute electronegativity of A in AB^+ as I_A, and the absolute electronegativity of B in AB^+ as I_B.

In the two-electron case, however, besides the atomic term and the electron-core integral, we must consider a two-electron energy integral representing the interaction of one electron in one atomic orbital with the other electron in the molecular orbital. That is, we must consider the screening of one electron by the other. Since the spin functions are antiparallel in the bonding orbital we have to take into account only the Coulomb integral and we write:

$$\begin{aligned} \alpha_A = \varepsilon_A &+ \int \bar{u}_b \chi_A^*(1) \chi_A(1) d\tau \\ &+ \int\int \chi_A^*(1) \chi_A(1) e^2/r_{12} \Psi^*(2) \Psi(2) d\tau_1 d\tau_2 \end{aligned} \tag{11}$$

* I venture to suggest that because these long papers are written in French (the English version is not generally available) they have been greatly overlooked, except with respect to the proposed approximations for the calculation of molecular integrals.

With regard to the two-center integrals Mulliken suggested the following approximation:* the MO charge distribution $\Psi^*\Psi$ is replaced by $\frac{1}{2}(\chi_A^*\chi_A + \chi_B^*\chi_B)$. The two-electron integral in (11) is substituted by $\frac{1}{2}(J_{AA} + J_{BB})$, where

$$J_{AA} = \int\int \chi_A^*(1)\chi_A(1)\frac{e^2}{r_{12}}\chi_A^*(2)\chi_A(2)d\tau_1 d\tau_2,$$

and

$$J_{AB} = \int\int \chi_A^*(1)\chi_A(1)\frac{e^2}{r_{12}}\chi_B^*(2)\chi_B(2)d\tau_1 d\tau_2.$$

After substitutions and allowance for a possible heteropolarity, equation (11) reads:

$$\alpha_A = \varepsilon_A + \int \bar{u}_b\chi_A^*(1)\chi_A(1)d\tau + \tfrac{1}{2}(1 - Q)(J_{AA} + J_{AB}). \quad (12)$$

Q, equal to the bond ionicity $(a^2 - b^2)$, is a complicated function of $(\alpha_A - \alpha_B)$, and of the overlap and bond integrals. If, instead of the core integrals $\int \bar{u}_b\chi_A^*\chi_A d\tau$, one considers *neutral atom integrals* $\int \bar{v}_b\chi_A^*\chi_A d\tau$, and since $\int \bar{v}_b\chi_A^*\chi_A d\tau - \int \bar{u}_b\chi_A^*\chi_A d\tau = J_{AB}$, equation (12) can be written:

$$\alpha_A = \varepsilon_A + \int \bar{v}_b\chi_A^*(1)\chi_A(1)d\tau - \tfrac{1}{2}(1 - Q)(J_{AA} - J_{AB}). \quad (13)$$

Again, considering only the difference $(\alpha_A - \alpha_B)$ and remembering that $J_{AB} = J_{BA}$, Mulliken writes:

$$\alpha_A - \alpha_B = A\left\{\left[\varepsilon_A + \int \bar{v}_b\chi_A^*\chi_A d\tau + \tfrac{1}{2}J_{AA}\right] - \left[\varepsilon_B + \int \bar{v}_a\chi_B^*\chi_B d\tau + \tfrac{1}{2}J_{BB}\right]\right\} \quad (14)$$

where A is a function of $(\alpha_A - \alpha_B)$, S_{AB}, and β_{AB}. Making the assumption that $\int \bar{v}_b\chi_A^*\chi_A d\tau = \int \bar{v}_a\chi_B^*\chi_B d\tau$, Mulliken defines the absolute electronegativity of an atom A in the molecule AB as:

$$X_A = -\alpha_A = -\varepsilon_A - \tfrac{1}{2}J_{AA}, \quad (15)$$

* This is the same as approximating the bicentric charge distribution $\chi_A^*\chi_B$ by $\frac{1}{2}(\chi_A^*\chi_A + \chi_B^*\chi_B)S_{AB}$, which represents a considerable simplification in the calculation of molecular integrals.[76]

and similarly:

$$X_B = -\alpha_B = -\varepsilon_B - \tfrac{1}{2}J_{BB}. \tag{16}$$

If one further adopts the approximations[79,90] $J_{AA} = I_A - A_A$, and $J_{BB} = I_B - A_B$, one finally gets:[45]

$$\begin{aligned} X_A &= I_A - \tfrac{1}{2}(I_A - A_A) = \tfrac{1}{2}(I_A + A_A) \\ X_B &= I_B - \tfrac{1}{2}(I_B - A_B) = \tfrac{1}{2}(I_B + A_B) \end{aligned} \tag{17}$$

It should be pointed out that, although the polarity depends on the difference $(\alpha_A - \alpha_B)$, the orbital energies and hence the bond energies depend of the sum $(\alpha_A + \alpha_B)$ as well. So molecular terms in the Coulomb integrals cannot simply be dropped in MO calculations. The molecular terms could, in principle, be partitioned in atomic contributions, but no unambiguous way of doing this has been found. The single-center expansion treatment of molecules[118] shows that, since the expansion center may be chosen as one of the nuclei, molecular energies can be described, as a limiting case, in terms of modified atomic orbitals, but on account of heavy technical difficulties this has not been done except for the simplest cases.[53] A limitation of Mulliken's treatment is its inability to allow for SCF, or, more strictly, SCCC (self-consistent charge and configuration) calculations. This results because the introduction of charge asymmetry is not made in a sufficiently flexible way. The substitution of the MO density $\Psi^*\Psi$ by $\frac{1}{2}(\chi_A^*\chi_A + \chi_B^*\chi_B)$ is reasonable only so long as the coefficients a and b in the MO are equal. The more general expression, $(a^2\chi_A^*\chi_A + b^2\chi_B^*\chi_B)$ should be used if SCCC calculations are intended. Such treatments of electronegativity have been described by Moffitt[79] and more recently by Klopman,[64] on the basis of Roothaan[112] SCF techniques. Before a discussion of these approaches it is interesting to review briefly the MO justifications for Pauling scale.[75,83,101] By expanding the lower root of the secular equation of the variational MO method, neglecting higher-order terms, and assuming that the arithmetic mean rule is valid one gets the following expression:

$$\begin{aligned} \Delta_{AB} = D_{AB} - \tfrac{1}{2}(D_{AA} + D_{BB}) &= -E_{AB} + \tfrac{1}{2}(E_{AA} + E_{BB}) \\ &= \frac{\tfrac{1}{4}(\alpha_A - \alpha_B)^2}{2[\beta_{AB} - \tfrac{1}{2}(\alpha_A + \alpha_B)S_{AB}]}. \end{aligned} \tag{18}$$

If one identifies the expression

$$\frac{\frac{1}{2}(\alpha_A - \alpha_B)}{\{2[\beta_{AB} - \frac{1}{2}(\alpha_A + \alpha_B)S_{AB}]\}^{\frac{1}{2}}}$$

with $(X_A - X_B)$, the Pauling equation, $\Delta_{AB} = (X_A - X_B)^2$, is obtained. With all simplifications made, the fact remains that to consider electronegativity as an atomic parameter is a bold step, not based in quantum-mechanical arguments, and that the Pauling scale must be considered as a useful empirical generalization.*

3. Moffitt's Approach

One of the fundamental problems of semiempirical LCAO-MO methods is the choice of the diagonal matrix elements. In many calculations[6,11,22,38,57,58,74,88,110a,128,134] the diagonal elements are taken as the VSIP's of the atoms, whereas in other calculations[7,14,20,61,66,91,101,110] the diagonal elements are identified with the electronegativities. In a few cases the terms of the Hamiltonian not centered in atom A have been taken into consideration, either as the electron-affinity of the bonded atom[42,46] or as the Madelung-Jørgensen energy.[102,103] Another fundamental problem is, of course, rendering the diagonal elements charge-dependent. Moffitt[79] in his elegant paper on molecular orbitals and the Hartree field tackled both problems. Moffitt proposed that the diagonal elements be given by the linear equation:

$$\alpha_A = \alpha_A(a^2) = -I_A + (I_A - A_A)a^2. \tag{19}$$

This equation is essentially an interpolation formula based on the atomic values for non-fractional values of the coefficient a: $\alpha_A = -I_A(a = 0)$, and $\alpha_A = -A_A(a = 1)$. Interpolating to the value $a = \sqrt{\frac{1}{2}}$, one obtains $\alpha_A = -\frac{1}{2}(I_A + A_A)$. Hence if a were the coefficient of χ_A in the MO, a covalent bond ($a = b$) would require $\alpha_A = \alpha_B$, and one would obtain $X_A = \frac{1}{2}(I_A + A_A)$. However, it is clear from Moffitt's paper that a (ω_i^2 in his notation) is not the coefficient of χ_A properly but of the remaining electron

* Pauling[100] has expressed the thought that the theory of resonance should be considered as a development of the chemical structural theory, and this is probably equally true with respect to his electronegativity scale.

of the MO in atom A. Moffitt's difficulty besets all SCCC calculations of one-electron models. Because the electron does not repel itself the repulsion energy between n degenerate electrons is $\frac{1}{2}n(n-1)J$, which is 0 if $n = 1$. This is the correct quantum-mechanical expression but exactly for this reason it is valid only for $n = 2a^2 = 0$, 1, and 2. But we need to have a charge-dependence scheme that can answer such chemically meaningful question as: what is the value of the diagonal matrix element α_A in a doubly occupied MO in which $a^2 < \frac{1}{2}$? A solution of these problems based on a reasonable, albeit arbitrary, partitioning of electron densities was recently proposed by Klopman.[64] Since it retains the basic features of Moffitt's treatment but goes further, we shall examine it.

4. Klopman's Approach. Electronegativity and Atomic Terms

Starting with the free atoms, Klopman recalls[21,122,127] that the total energy of a given atomic state can be written as the sum:

$$E_A = \sum_i B_A^l + \tfrac{1}{2}\sum_{ij} A_A^+ \delta_{ij} + \tfrac{1}{2}\sum_{ij} A_A^- (1 - \delta_{ij}), \qquad (20)$$

where B_A^l is the energy of an electron i in the atomic spin-orbital χ_A in the field of the core and in the absence of interactions with other electrons in the same shell (l is the azimuthal quantum number), A_A^+ is the interaction energy between electrons with the same spin, A_A^- is the interaction energy between electrons with opposite spins, and δ_{ij} is Kronecker symbol. If the electrons belong to the same orbital, equation (20) reduces to:

$$E_A = \sum_i B_A + \tfrac{1}{2}\sum_{ij} A_A^- (1 - \delta_{ij}) \qquad (21)$$

or:

$$E_A = nB_A + \tfrac{1}{2}n(n-1)J_{AA}, \qquad (22)$$

where n is the occupation number of the bonding spin-orbital ($0 < n < 2$). Klopman correctly points out that the energy of an atomic spin-orbital is a non-continuous function of n and that therefore it is non-differentiable with respect to n. From equation (22) the atomic terms for the isolated atom can be seen to be $-I_A$ for the first electron and $-A_A$ for the second. Note, however, that if $n < 1$ the repulsion term $\frac{1}{2}n(n-1)J_{AA}$ does not

vanish, indicating that the occupation number n should be interpreted as a *geminal occupation number*. This is an important point, connected with, for example, the fact that in a homonuclear diatomic molecule, say H_2, the time-average occupation number of each atomic oribtal is 1 and yet, because of the presence of the second electron with opposite spin, the atomic term is not $-I_H$. It should be pointed out that $\frac{1}{2}n(n-1)J_{AA}$ is negative for $n < 1$, which corresponds to an attractive potential for the electron–electron interaction (!). The author is now strongly reserved with regard to the use of equations (22) or (23) for non-integral values of n.

Klopman's equations justify the concept of atomic orbital electronegativity recently proposed by Iczkowski and Margrave,[60] Klixbull Jørgensen,[62] and Hinze, Whitehead, and Jaffe.[55] It is well known[12,28,47] that successive ionization potentials can be expressed reasonably well as a power function of the charge in the atom. In the range A^{-1} to A^{+1}, involving a given atomic orbital, a parabolic relation can be used:

$$E(n) = a_1 n + b_1 n^2. \tag{23}$$

For the stated conditions equation (23) is identical with (22). The constants a_1 and b_1 can be obtained from the experimental values of E(n) for the integral values of the occupation number n: $E(1) = -I$, $E(2) = -(I + A)$, where I and A are the valence-state term values. One obtains $a_1 = -\frac{1}{2}(3I - A)$ and $b_1 = \frac{1}{2}(I - A)$. If we assume that E(n) is a continuous and differentiable function of n in the interval $0 < n < 2$ we obtain $(dE/dn)_{n=1} = -\frac{1}{2}(I + A)$. This is an important result and it enables us to define electronegativity as the potential acting in a half-filled atomic orbital.

We wish to emphasize that E(n) represents the energy of an orbital, not of an electron in that particular orbital. In fact, the energy of an electron in a central field orbital cannot be represented by a square function of the charge, but requires a linear function.[126] The parabolic relation (23) can be understood only if a second electron is present, and only under this condition can we proceed from (22) to (23). Hence, equation (23) refers to the energy of a geminal, and electronegativity defined as $(dE/dn)_{n=1}$ is a *geminal electronegativity*. Thus, electronegativity is a concept

intimately connected with the idea of electron-pair functions and it seems that the importance of the Lewis electron pair[69] has a remarkable permanence.[120] As long as we are interested in collective properties (bond energies, bond distances, etc.) molecules are, to a very good approximation, made of atomic cores and electron pairs. It is to be expected that a workable two-electron MO method will be a much more powerful tool than any one-electron description.[92] One is tempted to say, paraphrasing a famous American politico, that what quantum chemistry needs is a good two-electron theory. The electron-pair concept will probably survive the idea of two-center bonds. The existence of electron-deficient compounds requires modification of Lewis electron pair rule to: a chemical bond is the sharing of electron pairs among two or more atomic cores.[52,72,105,113,114] It is interesting that, although Linnett's double-quartet description[71] has many interesting features, apparently it does not lead to an interpretation of bond polarity, which is the property most intimately connected with electronegativity.

From equation (23) a linear relation between electronegativity and charge is obtained:

$$X(n) = dE/dn = -\tfrac{1}{2}(3I - A) + (I - A)n. \qquad (24)$$

Since electronegativity according to equation (24) can be interpreted as a potential, it was postulated that in a chemical bond the occupation numbers of the valence orbitals change until the potential acting on the electron pair with respect to the cores A^+ and B^+ is the same.[55] This is essentially Sanderson's *principle of electronegativity equalization*.[115,116] Because molecular terms also change with charge transfer from one atomic orbital to another, this principle is not strictly valid: it is the total energy of the molecule which must be at a minimum for the equilibrium charge distribution.[62,64,102] In other words, the equalization of electronegativities would be attained only if the atoms were separated by an infinite distance. As a result the charge distribution calculated from the principle of electronegativity equalization is invariant with respect to bond distance, obviously an absurd result.[41]

The principle of electronegativity equilibration is preserved, under a modified form, by Klopman's treatment of molecules.

Since an orbital-occupation number of 1 corresponds to $a^2 = \frac{1}{2}$, equation (21) for an atomic orbital in a homonuclear molecule is (if we disregard polycentric terms):

$$E_A = \sum_i n_i B_A + \tfrac{1}{2} \sum_i \sum_j n_i n_j A_A^- (1 - \delta_{ij}). \tag{25}$$

Hence the *neutral electronegativity* of an atom A in a molecule is:

$$X_A = B_A + \sum_{j \neq i} n_j A_A^-. \tag{26}$$

This result is also obtained from the expression for the MO energy of homoatomic systems from the condition $\partial E/\partial a = \partial E/\partial b = 0$, as required by the variation principle. In the homonuclear case the electron–electron repulsion term in equation (26) can be partitioned by assuming that half of it is the electron–electron repulsion integral for two electrons centered in A, that is, $\frac{1}{2}J_{AA}$. If this is done, then, assuming that $J_{AA} = (I_A - A_A)$ and collecting the center A terms in a single term, one obtains:

$$\alpha_A = -\tfrac{1}{2}(I_A + A_A) + \partial E^M/\partial a, \tag{27}$$

where $\partial E^M/\partial a$ refers to the variation in molecular-energy integrals other than the center *A* terms. For heteroatomics Klopman assumes that the point-charge description of non-bonding interactions is correct[108] and, further, in computing the occupation numbers of atomic orbitals one counts 1 for each non-bonding electron and $\frac{1}{2}$ for each electron participating in the bond. It is a gratifying aspect of this approach that electronegativities appear in a natural way in the diagonal matrix elements. Equalization of atomic electronegativities does not occur, but since the electron population of the orbitals corresponds to a minimum in the total molecular energy, Klopman calls these orbitals *equipotential orbitals*.

5. Diagonal Matrix Elements, Electronegativity, and Madelung-Jørgensen Energy

The energy of a normalized MO described by $\Psi = a\chi_A + b\chi_B$ is given by $\varepsilon_{MO} = \int \Psi^* \mathfrak{H} \Psi d\tau$, and if χ_A and χ_B are also normalized one has:

$$\varepsilon_{MO} = a^2 \int \chi_A^* \mathfrak{H} \chi_A d\tau + b^2 \int \chi_B^* \mathfrak{H} \chi_B d\tau + 2ab \int \chi_A^* \mathfrak{H} \chi_B d\tau. \tag{28}$$

When we repeat Mulliken's analysis with the explicit expression for the molecular orbital density $\Psi^*\Psi = a^2\chi_A^*\chi_A + b^2\chi_B^*\chi_B$, the diagonal elements are given by:

$$\alpha_A = \int \chi_A^* \mathfrak{H} \chi_A d\tau = -I_A + \int \bar{u}_b \chi_A^* \chi_A d\tau + a^2 J_{AA} + b^2 J_{AB}. \quad (29)$$

The physical meaning of each term in the above equation is clear from Mulliken's treatment. Let us recall that the sum $a^2J_{AA} + b^2J_{BB}$ replaces the integral describing the repulsion of an electron in χ_A by the other electron in the MO. Integrals of the type $\iint \chi_A^*(1)\chi_B^*(2)e^2/r_{12}\chi_A(1)\chi_B(2)d\tau_1 d\tau_2$ appear in the off-diagonal elements only, and Mulliken has shown[85] that they are small.

Further approximations can now be made in expression (29) to render it more convenient for SCCC calculations in which the electron–electron interactions are included in the diagonal elements in some average way. If $a = b = 1/\sqrt{2}$, the diagonal element (29) reduces to:

$$\begin{aligned} \alpha_A &= -I_A + \tfrac{1}{2}(I_A - A_A) + \int \bar{u}_b \chi_A^* \chi_A d\tau + \tfrac{1}{2} J_{AB} \\ &= -X_A + \int \bar{u}_b \chi_A^* \chi_A d\tau + \tfrac{1}{2} J_{AB}. \end{aligned} \quad (30)$$

We now make the usual assumption of perfect screening by the non-bonding electrons[108] and we also write $\int \bar{u}_b \chi_A^* \chi_A d\tau = -e^2/r_{AB}$, and $J_{AB} = e^2/r_{AB}$, where r_{AB} is the bond distance in AB. Thence, for homopolar bonds we obtain:

$$\alpha_A = -X_A - e^2/2r_{AB} = -(X_A + e^2/2r_{AB}). \quad (31)$$

We can see that the diagonal elements of homopolar molecules are given, to a good approximation, by the sum of the electronegativity and the term $e^2/2r_{AB}$; the latter is the *Madelung-Jørgensen energy per electron.** For example, in the case of the C–C π-bond in ethylene ($r_{CC} = 1.334$ Å)[8], if one uses the valence-state data of Pilcher and Skinner,[104] one finds, according to (31),

* The Madelung-Jørgensen energy is the electrostatic energy between charged particles. Its importance within this context was first pointed out by Klixbüll Jørgensen,[62] who called it the Madelung energy because it is an important term in ionic crystals, where it appears multiplied by the Madelung constant for the crystal.

$\alpha_C = -11.83$ eV, whereas $-I_C = -11.22$ eV and $-(I_C + A_C) = -11.84$ eV. We have here a possible justification for the use of the neutral-atom VSIP or of the sum $(VSIP)_A + (VSEA)_B$ as the carbon, hydrogen, and nitrogen diagonal matrix elements in MO calculations of organic molecules.[42,46,58]

In the limiting case $A^-B^+(a = 1, b = 0)$, equation (28) reduces to $\varepsilon_{MO} = \alpha_A = \int \chi_A^* \mathfrak{H} \chi_A d\tau$, and from (29) one gets $\alpha_A = -A_A + \int \bar{u}_b \chi_A^* \chi_A d\tau$. Replacing the electron-core attraction integral by $-e^2/r_{AB}$, we can write $\alpha_A = -A_A - e^2/r_{AB}$. Since in this purely ionic situation the covalent bond order, 2ab, is zero, α_A must be equal to the energy of an electron in the highest occupied MO, that is, must be equal to the ionization potential of A^-B^+. It is not surprising,[128] therefore, that the ionization potential of a highly polar molecule such as KI(g) is much greater* than the electron–affinity of the gaseous ion I^-.

Finally, if $a = 0$, corresponding to the extreme structure A^+B^-, $\alpha_A = -I_A + \int \bar{u}_b \chi_A^* \chi_A d\tau + J_{AB} = -I_A$. However, in the energy expression (29) α_A appears multiplied by a^2 and thus it does not contribute to the MO energy.

Equation (29) can now be written in the form:

$$\alpha_A = -I_A + \tfrac{1}{2} n_A (I_A - A_A) - e^2/r + \tfrac{1}{2}(2 - n_A) e^2/r, \quad (32)$$

where $n_A = 2a^2$ is the occupation number of χ_A in the MO, and the point-charge model is assumed to be valid. We obtain, of course, $\alpha_A = -I_A (n_A = 0)$, $\alpha_A = -(X_A + e^2/2r)(n_A = 1)$, and $\alpha_A = -(A_A + e^2/r)(n_A = 2)$. The interesting point, however, is that for the usual range of bond distances equation (32) leads to a very slight dependence of α_A on n_A. Consider, for example, the case of the integral α_C in a C–N π-bond 1.37 Å in length. The values are: $\alpha_{C^+} = -11.22$ eV, $\alpha_C = -11.15$ eV, and $\alpha_{C^-} = 11.08$ eV. Similar results were recently obtained by Jørgensen, Horner, Hatfield, and Tyree (personal communication from Professor C. K. Jørgensen).

The dependence between the diagonal element and the orbital population is not only slight but linear. Now, a linear function between the Coulomb integral and atomic charge has been very

* The ionization potential of gaseous KI is[43] 8.3 ± 0.2 eV. The calculated value for the structure $K^+I^-(-A_A - e^2/r_{KI})$ is 8.0 eV.

much used in simple LCAO-MO calculations of organic substances since the paper by Wheland and Mann.[123,133] On the other hand, we have seen that the energy of an atomic orbital in a free atom is a square function of the orbital population, provided we consider the electron-pair as a fundamental entity. The contradiction is eliminated, however, if we recall that in the energy expression [equation (28)] the diagonal matrix elements appear multiplied by the coefficients squared (a^2 and b^2), that is, by the atomic-orbital populations.

Although it is the Reviewer's feeling that, at this stage, calculations of bond energies by semi-empirical SCCC-MO methods are always open to criticism, mainly because of the uncertainties in core–core repulsion potentials, off-diagonal matrix elements, etc., the point-charge model is, in fact, a better approximation than most people would think. In fact, a comparison of the available values of the core integral $\int \bar{u}_b \chi_A^* \chi_A d\tau$ with the simple point-charge value $-e^2/r$ shows that for the equilibrium bond distances the two sets of values differ by less than 10 per cent. Calculations of energy levels in transition-metal complexes along the lines suggested here are being tried in Professor Gray's laboratory at Columbia University. There can be little doubt that at the moment the most sensible approach to an MO description of complexes is the SCCC-MO method first applied by Ballhausen and Gray[6] to the $VO(H_2O)_5^{2+}$ ion. It seems, however, that the diagonal elements are treated as very steep functions of the atomic charges and that if the iteration is carried out also with respect to the ligands it will lead to difficulties in convergence.

The question may be asked whether from equation (29) it is possible to obtain for the bond energy, $E_{AB} = 2\varepsilon_{MO} + I_A + I_B +$ core repulsion, an expression involving, as does the VB description, a covalent bond energy plus an ionic bond energy. The answer is no, except for the limiting case of a pure ionic bond A^-B^+. The reason is that in using the approximate wave-function (4), instead of the more complete wave-function (1), we lost the one-to-one correspondence between the VB wave function and the MO wave function. Consequently, the atomic terms A_B and I_A cannot appear in the equations. Considering the two-electron function

$$\Psi = [a\chi_A(1) + b\chi_B(1)][a\chi_A(2) + b\chi_B(2)],$$

and expanding, we find:

$$\Psi = a^2\chi_A(1)\chi_A(2) + b^2\chi_B(1)\chi_B(2) + ab[\chi_A(1)\chi_B(2) + \chi_A(2)\chi_B(1)].$$

If $a^2 \gg b^2$, the above equation can be written as:

$$\Psi = ab(2 + 2S_{AB}^2)^{\frac{1}{2}}\Phi_2 + a^2\Phi_1. \tag{33}$$

But, as pointed out by Warhurst,[132] if $a^2 \gg b^2$, $a^2 \gg ab(2 + 2S_{AB}^2)^{\frac{1}{2}}$; in other words, the correspondence between the two descriptions is reasonable only for the extremely ionic case A^-B^+.

One final word of caution: Calculations of the electronic energy of doubly occupied molecular orbitals involve, besides the difficulties already mentioned and associated with the evaluation of off-diagonal elements, of core–core repulsions, etc., problems connected with the electron–electron interactions in the evaluation of the diagonal elements. The energy of two electrons in a MO is the sum of the energies involved in the processes, (1) $AB - e \rightarrow AB^+$, and (2) $AB^+ - e \rightarrow AB^{2+}$. But the Hamiltonians of (1) and (2) are different, since there is no screening potential in (2). Let us consider the ionic case A^-B^+, where the VB-MO correspondence holds. We know that in this case the bond energy is given by:

$$E_{AB} = -e^2/r_{AB} - A_A + I_B + (\text{exponential term}).$$

This result can be obtained from the MO equation (29) only if, instead of taking the energy of the two electrons in the MO as $2\varepsilon_{MO}$, one uses for α_A of the first electron the expression given by (30), but for the second electron the expression (10). We write:

$$\begin{aligned}\varepsilon_{(2e)} = {} & a^2\left[-I_A + \int \bar{u}_b\chi_A^*\chi_A d\tau + a^2J_{AA} + b^2J_{AB}\right] \\ & + a^2\left[-I_A + \int \bar{u}_b\chi_A^*\chi_A d\tau\right] + b^2\left[-I_B + \int \bar{u}_a\chi_B^*\chi_B d\tau\right. \\ & \left. + b^2J_{BB} + a^2J_{AB}\right] + b^2\left(-I_B + \int \bar{u}_a\chi_B^*\chi_B d\tau\right) \\ & + 2ab(\beta_{AB} + \beta_{AB} +)\end{aligned} \tag{34}$$

Since $a^2 = 1$, and making the usual substitutions for the electron–core attraction integrals and the electron–electron repulsion integrals, we obtain:

$$\begin{aligned}\varepsilon_{(2e)} &= -I_A - e^2/r_{AB} + (I_A - A_A) - I_A - e^2/r_{AB} \\ &= -I_A - A_A - 2e^2/r_{AB}.\end{aligned} \tag{35}$$

Hence:

$$E_{AB} = -I_A - A_A - 2e^2/r_{AB} + I_B + I_A + (\text{repulsion term}). \quad (36)$$

The repulsion term, however, can be written as the sum of an electrostatic term, e^2/r_{AB}, plus an exponential term. Hence:

$$E_{AB} = -e^2/r_{AB} - A_A + I_A + (\text{exponential term}). \quad (37)$$

It is seen that in the only case where a one-to-one correspondence is expected, that is, when $a = 1$, the MO and the VB description give the same result.

Everything we have said in this section is valid only for the approximate MO theories in which the effect of the two-electron operators can be incorporated with the nuclear attraction in an effective one-electron potential (core field potential). The resulting MO's are the one-electron eigenfunctions of the core field. Within this scheme the concept of electronegativity can be introduced in a natural way. However, because of its close connections with the pair-function concept, this type of treatment is valid only for closed-shell systems. Applications to open-shell cases (free radicals, odd molecules, excited electronic states, etc.) are not straightforward. Explicit inclusion of interelectronic interactions can be made, in principle, by Roothaan technique,[112] perhaps in the approximate Pariser-Parr-Pople form.[92] But then the hope of conserving the concept of electronegativity is lost.

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VARIATIONAL THEORY OF REACTION RATES

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I. INTRODUCTION

The variational theory of reaction rates provides a systematic method for making and improving estimates of reaction rates for systems that can be described classically. It is based on an approach originally used by Marcelin[1] in 1915 and later developed in detail by Wigner,[2] Horiuti,[3] and the writer.[4] The basic assumption

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of the theory is that a reacting system can be described by the motion of a representative point in the phase space of the system. This phase space is then divided by a trial surface into regions corresponding approximately to the reactants and the products, and the rate at which representative points flow through the surface in one direction is calculated. Clearly, such a calculation gives an upper limit to the true reaction rate since passage at least once through the trial surface is a necessary condition for reaction. Finally, the trial surface is varied to obtain the minimum flow rate, which is the best approximation to the true reaction rate for the given range of variations.

In principle, this procedure can lead ultimately to the true reaction rate since it can be seen from the flow analogy that there exists a set of surfaces that are crossed once and only once by all trajectories leading from reactants to products. In practice, even for three-body reactions, the surfaces corresponding to the true rate are, in general, much too complicated to be dealt with analytically, and we must hope that reasonable approximations can be found. In this connection it should be noted that there is at least one important special case in which the trial surfaces may be relatively simple. This occurs when the collisions between particles are impulsive, so that recrossing of the surfaces becomes negligible. Under these conditions the variational theory gives results in agreement with those obtained from the impulse approximation.

The variational theory is very general in its applications and includes as special cases many of the more familiar classical and semiclassical theories of reaction rates. We shall, therefore, review the basic assumptions on which the theory is based.

The first of these assumptions is that the reactions can be described by using classical mechanics. Although the conditions for this cannot be stated precisely, a rough general criterion is that the reduced wavelength $\lambda\!\!\!^{-}$ of the interacting particles should be small compared with the characteristic length in which appreciable changes in the potential occur. For atomic and molecular interactions, this may be taken as the Bohr radius a_0, and we obtain the condition:

$$\lambda\!\!\!^{-}/a_0 = (I_H m_e/E_k M)^{\frac{1}{2}} < 1, \tag{1.1}$$

where I_H is the ionization potential of hydrogen, m_e is the electron mass, and E_k and M are the kinetic energy and mass of a typical particle. This inequality indicates that, for all particles heavier than hydrogen, classical mechanics should be a reasonable approximation for energies above 10^{-2} eV or temperatures above 100°K. It is pointless to argue about how much less than unity $\lambda\!\!\!^{-}/a_0$ should be because the division between classical and quantum mechanics is not precise, and in practice it is usually found that, where appreciable averaging of the results is involved, classical mechanics are valid well into the quantum-mechanical domain.

The second assumption is that the interactions between particles can be described by a potential which is a unique function of the relative position coordinates. For atomic and molecular interactions this requires that the Born–Oppenheimer separation shall be valid, so that electronic transitions are forbidden. Although it is now recognized that there are many important exceptions to this rule, it is still expected to hold for a large class of chemical reactions.

The final assumption is that the reacting systems are independent of each other, so that ensemble averages may be taken. For reactions occurring in bulk media, this requires that the systems are sufficiently dilute for the effective range of the interactions to be small compared with the interparticle spacing. An equivalent statement is that the mean free path λ_p of a particle must be large compared with the range of the interaction. This leads to the condition

$$a_0^3 N \sim a_0/\lambda_p \ll 1, \tag{1.2}$$

where N is the particle number density. This is true for most gases away from the critical point.

On the basis of these assumptions, we may now proceed with the formal mathematical development of the variational theory. This is given in Section II. In Section III we use the results of Section II to derive some of the more familiar theories of reaction rates. In Section IV we consider the applications of the theory to the problem of three-body recombination and dissociation, and in the final Section we discuss briefly corrections and extensions of the theory.

II. BASIC EQUATIONS

Consider an ensemble of systems each containing n classical particles interacting with a known potential. The state of each system can be represented by a point in a $3n$-dimensional phase space, the axes of which are the conjugate momentum and position coordinates $(\mathbf{p},\mathbf{q})$ of the particles. Let $\rho(\mathbf{p},\mathbf{q})$ be the density of such representative points. Then, since the number of points is conserved, ρ satisfies the equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0, \tag{2.1}$$

where $\mathbf{v}$ is the generalized velocity of a point in phase space and ∇ is the generalized divergence operator. If the Hamiltonian of the systems is $H(\mathbf{p},\mathbf{q})$, the components of $\mathbf{v}$ may be obtained from the equations

$$\dot{q}_i = \partial H/\partial p_i, \qquad \dot{p}_i = -\partial H/\partial q_i. \tag{2.2}$$

These equations determine the flow pattern of points in phase space which move as though they were entrained in an incompressible fluid. This analogy is extremely useful and permits one to describe a chemical reaction as the convection of representative points from one region of phase space to another by the incompressible phase fluid.

We now consider a volume $\Omega(i)$ in phase space corresponding to a particular chemical state i of our system. Integrating (2.1) over this volume we obtain

$$\partial N(i)/\partial t = -\int_{\Omega(i)} (\nabla \cdot \rho \mathbf{v}) \prod_1^{3n} dp_j dq_j, \tag{2.3}$$

where

$$N(i) = \int_{\Omega(i)} \rho \prod_1^{3n} dp_j dq_j \tag{2.4}$$

is the number of systems in the state i. The right-hand side of eqn. (2.3) may now be converted into a surface integral, so that

$$\partial N(i)/\partial t = -\int_{S(i)} \rho(\mathbf{v} \cdot \mathbf{n}) ds, \tag{2.5}$$

where $\mathbf{n}$ is the unit outward normal to ds and $S(i)$ is the surface

bounding $\Omega(i)$. Equation (2.5) merely states that the rate of change of systems in $\Omega(i)$ is equal to the negative of the rate at which they flow out across its boundary.

A. The Reaction Rate

We may now further decompose the surface integral in (2.5) into terms representing the population and depopulation of the state i by reactions leading to and from various final states f. When this is done, eqn. (2.5) becomes

$$\partial N(i)/\partial t = \prod_f [R(i,f) - R(f,i)], \tag{2.6}$$

where

$$R(f,i) = \int_{S(f,i)} \rho(\mathbf{v} \cdot \mathbf{n}) ds \tag{2.7}$$

and $S(f,i)$ is that part of the boundary between i and f on which $(\mathbf{v} \cdot \mathbf{n}) > 0$. Note that $R(f,i)$ is the total rate at which representative points cross the boundary between i and f in one direction. Clearly $R(f,i)$ gives an upper limit to the net reaction rate since all systems which react must cross $S(f,i)$ at least once. It is also clear from the flow analogy that there exists a set of surfaces which are crossed once and only once by trajectories leading from i to f. However, to find these surfaces, one would, in general, have to solve the equations of motion (2.2), and this cannot usually be done. We therefore propose instead to carry out the integration of (2.7) over various trial surfaces and to select the smallest crossing rate as the best approximation to the true reaction rate. This procedure may be carried out either by trial and error or by selecting surfaces depending on a set of parameters which may be varied to yield a minimum rate.

We now wish to obtain an explicit expression for $R(f,i)$ in terms of the canonical coordinates $(\mathbf{p},\mathbf{q})$. Let the partial surface $S(f,i)$, corresponding to reactions leading from i to f, be defined by the set of constraints

$$S(\mathbf{p},\mathbf{q}) = 0, \qquad C(\mathbf{p},\mathbf{q}) < 0, \qquad (\mathbf{v} \cdot \mathbf{n}) > 0, \tag{2.8}$$

which determine respectively the boundary of $\Omega(i)$, the boundary of the final channel, and the direction of flow. The normal to $S(f,i)$ can then be expressed

$$\mathbf{n} = (\nabla S/|\nabla S|)_{S=0}, \tag{2.9}$$

and substitution of this into expression (2.7) gives

$$R(f,i) = \int_{S(f,i)} \rho(\mathbf{v} \cdot \nabla S) |\nabla S|^{-1} ds. \tag{2.10}$$

To obtain the Wigner form of the reaction rate, we substitute

$$\mathbf{v} \cdot \nabla S = dS/dt \tag{2.11}$$

into (2.10), then integrate and differentiate with respect to dS. This yields

$$R(f,i) = \left(\frac{d}{dx} \int^{x} \int_{S(f,i)} \rho \left(\frac{dS}{dt} \right) \frac{ds dS}{|\nabla S|} \right)_{x=0}. \tag{2.12}$$

Since $|\nabla S|^{-1} dS$ is just the differential element of length perpendicular to ds, the factor

$$|\nabla S|^{-1} dS ds = \prod_{1}^{3n} dp_j dq_j \tag{2.13}$$

in (2.12) is the volume element in phase space and (2.12) can be written:

$$R(f,i) = \left(\frac{d}{dx} \int_{\Omega(x)} \rho \left(\frac{dS}{dt} \right) \prod_{1}^{3n} dp_j dq_j \right)_{x=0}, \tag{2.14}$$

where volume of integration $\Omega(x)$ is defined by $S < x$, $C < 0$, and $dS/dt > 0$.

An alternative form of the result may also be obtained from (2.10) by using the equation

$$\mathbf{v} \cdot \nabla S = \prod_{1}^{3n} J_j, \tag{2.15}$$

where

$$J_j = \left(\frac{\partial H}{\partial p_j} \cdot \frac{\partial S}{\partial q_j} - \frac{\partial H}{\partial q_j} \cdot \frac{\partial S}{\partial p_j} \right) = \frac{dH dS}{dp_j dq_j} \tag{2.16}$$

is the Jacobian of the transformation from (H,S) to (p_j,q_j). Substituting (2.15) in (2.10) and using (2.13), we find

$$R(f,i) = \int_{S(f,i)} \rho \left(\sum_{1}^{3n} J_j / |J_1| \right) dH \prod_{2}^{3n} dp_j dq_j, \tag{2.17}$$

which is the form derived by the writer.[4] It is equivalent to carrying out the indicated differentiation in (2.14) and is usually a more convenient starting point for calculations.

B. Ignorable Coordinates

In the absence of external forces, the Hamiltonian $H(\mathbf{p},\mathbf{q})$ will be independent of the position of the center-of-mass $\mathbf{R}$ and the Euler angles ω_L and ϕ_L, corresponding to rotation of the system about the total angular momentum L and its z-component M. We may also expect the chemical state of the system and hence the function $S(\mathbf{p},\mathbf{q})$ to be independent of these coordinates. As a consequence, the corresponding Jacobians will all be zero, and (2.17) can be written

$$R(f,i) = \int \langle \rho \rangle \, \Gamma(f,i) dH d\mathbf{P} d\mathbf{R} dL d\omega_L dM d\phi_L, \tag{2.18}$$

where

$$\Gamma(f,i) = -\Gamma(i,f) = \int_{S(f,i)} \Big(\sum_{1}^{3n-5} J_j/|J_1| \Big) \prod_{2}^{3n-5} dp_j dq_j \tag{2.19}$$

is the rate of flow of phase fluid across the surface $S(f,i)$ for fixed H, $\mathbf{P}$, $\mathbf{R}$, L, ω_L, M, and ϕ_L, and

$$\langle \rho \rangle = \Gamma^{-1}(f,i) \int_{S(f,i)} \rho \Big(\sum_{1}^{3n-5} J_j/|J_1| \Big) \prod_{2}^{3n-5} dp_j dq_j \tag{2.20}$$

is the mean value of the density on the surface averaged with respect to the flow rate.

If additional constants of the motion (corresponding to ignorable coordinates) are known, the averaging of ρ may be restricted further. This will frequently be the case when the surface $S(f,i)$ is taken outside the region of strong interactions, and we shall consider some specific examples of this later. In general, however, no further reduction of expression (2.18) is possible without the introduction of specific assumptions concerning the Hamiltonian, the trial surface, or the density in the initial state, and (2.17) and (2.18) are the basic equations for estimating reaction rates.

C. Electronic Degeneracy

In deriving eqns. (2.17) and (2.18), we have tacitly assumed that the initial state of the system is non-degenerate. This is rarely the case, and there are usually several electronic configurations of the same energy which give rise to different interaction potentials. It is therefore necessary to multiply the rate for a given interaction potential (V_0) by the probability (f) that a system

in the initial state is moving on that particular potential curve. This may be expressed

$$f = g(V_0)/g(i), \tag{2.21}$$

where $g(V_0)$ is the electronic degeneracy associated with V_0 and $g(i)$ is the total degeneracy of the initial state. For simplicity we shall continue to omit this factor in our general considerations, but it must be taken into account in any explicit calculations.

D. General Rate Constant

To remove the dependence of the calculated rates on the concentration of the reactants, it is customary to express the results in terms of a reaction rate constant. The rate constant is defined as the reaction rate per unit volume divided by the product of the concentrations of the reactants. If the reaction is the result of the interaction of ν independent particles (where $\nu \leqslant n$), the reaction is said to be of order ν, and the rate constant is given by

$$k(f,i) = R(f,i)/V\prod_1^{\nu}[M_j], \tag{2.22}$$

where V is the normalization volume in configuration space and $[M_j]$ is the concentration of particles of type M_j in the initial state.

As a consequence of our assumption that the particles are independent, the density ρ in the initial state can be separated as a product of the densities ρ_j for the individual particles. Thus (2.4) for the total number of systems in the initial state can be written

$$N(i) = \int_{\Omega(i)} (\prod_1^{\nu}\rho_j)\prod_1^{3n} dp_j dq_j = V^{\nu}\prod_1^{\nu}[M_j]. \tag{2.23}$$

Combining eqns. (2.22) and (2.23), we obtain

$$k(f,i) = R(f,i)V^{\nu-1}/N(i) \tag{2.24}$$

as our expression for the rate constant of a reaction involving ν distinguishable particles proceeding at the rate $R(f,i)$ in a volume V. As can be seen from eqn. (2.6), $R(f,i)/N(i)$ has the dimensions of a reciprocal time, and hence (2.24) has the appropriate dimensions for a rate constant. For (2.24) to be valid, the calculated results must be independent of the normalization volume. As

will be seen below, this means that interactions between the particles must fall off sufficiently rapidly to make the reaction rate converge or that an artificial cut-off must be introduced.

E. Equilibrium Rate Constant

To calculate a bulk rate constant by means of the above equations, one must know the density ρ on the surface $S(f,i)$. For systems which are not in full thermodynamic equilibrium, this requires a solution of an appropriate master equation. However, in many systems which are out of chemical equilibrium, it may still be reasonable to suppose that the internal degrees of freedom of the reactants are in local equilibrium and can therefore be described by a Boltzmann distribution

$$\rho = \rho_0 e^{-H/kT}. \tag{2.25}$$

This assumption has been made in virtually all existing theories of bulk chemical reaction rates and leads to what may be called equilibrium rate constants.

Combining (2.25), (2.24), (2.17), and (2.4) and integrating over the center-of-mass coordinates, we obtain the following expression for the equilibrium rate constant:

$$k_e(f,i) = Q^{-1}(i) \int_{S(f,i)} e^{-E/kT} \Big(\sum_1^{3n-3} J_j/|J_1| \Big) dE \prod_2^{3n-3} dp_j dq_j, \tag{2.26}$$

where

$$Q(i) = V^{1-\nu} \int_{\Omega(i)} e^{-E/kT} \prod_1^{3n-3} dp_j dq_j \tag{2.27}$$

is the classical partition function per unit volume for a system in the initial state and

$$E = H - P^2/2M \tag{2.28}$$

is the total energy in the center-of-mass. Note that the identification of $Q(i)$ as the partition function requires that the variations of $S(f,i)$ be so restricted that the value of $Q(i)$ does not differ appreciably from the usually accepted value of the partition function. This criterion, in fact, determines the acceptable range of surfaces which may be used.

III. COMPARISON WITH CONVENTIONAL THEORIES

Before proceeding to the newer and more unique applications of the variational theory, it is instructive to investigate its relationship to some older and more familiar theories of chemical reaction rates. Almost all of these are based on the assumption of a Boltzmann distribution for the reactants, and of trial surfaces separating reactants and products that depend only on the coordinates in configuration space. The differences (which can be substantial) between various theories are due primarily to the particular trial surfaces chosen, and it is here that the variational theory provides both a connecting link and a criterion for selection.

A. Unimolecular Decay Theory

In the theory of unimolecular decay as developed by Slater,[5] it is assumed that an activated molecule will dissociate when a particular coordinate q_1 reaches a high value q. Thus the trial surface is defined by

$$S = q_1 - q = 0, \tag{3.1}$$

and the only nonvanishing Jacobian in eqn. (2.26) is

$$J_1 = \partial E/\partial p_1 = q_1. \tag{3.2}$$

Substituting (3.1) and (3.2) into (2.26) and (2.27), we obtain the high-pressure rate constant

$$k^\infty = Q^{-1} \int_{\dot{q}_1>0} \mathrm{e}^{-E^*/kT} q_1 dp_1 \prod_2^{3n-3} dp_j dq_j, \tag{3.3}$$

where

$$Q = \int \mathrm{e}^{-E/kT} \prod_1^{3n-3} dp_j dq_j \tag{3.4}$$

and E^* is the energy on the surface $q_1 = q$. Equation (3.3) is just Pelzer's formula in the general form derived in Chapter 9 of Slater's book.

B. Theory of Absolute Reaction Rates

In the theory of absolute reaction rates as developed by Eyring and his collaborators,[6] it is assumed that a chemical reaction can

be described as a flow of representative points over a saddle point in the potential energy of the system from a valley representing the reactants to one representing the products. A reaction coordinate q_1 parallel to the bottom of the valley is defined, and the flow rate through a surface perpendicular to q_1 located at the saddle point is then calculated, a Boltzmann distribution for the reactants being assumed. A variational version of the theory has also been proposed by Horiuti,[3] who points out that the best location for the surface is not necessarily at the saddle point but rather at the point where the flow rate through the surface is a minimum.

Following Horiuti, we introduce a surface $S(f,i)$ between reactants and products that spans the potential energy valley. We then chose as our coordinate system an orthogonal curvilinear set of q's with q_1 perpendicular to $S(f,i)$. Under these conditions the energy of the system is

$$E = p_1^2/2\mu_1 + E^*, \tag{3.5}$$

where p_1 and μ_1 are respectively the momentum and reduced mass corresponding to q_1, and the only non-vanishing Jacobian in (2.26) is

$$J_1 = \partial E/\partial p_1 = q_1. \tag{3.6}$$

Substituting (3.5) and (3.6) in (2.26) and integrating over p_1, we obtain

$$E = kTQ^{-1}\int_{S(f,i)} e^{-E^*/kT} \prod_2^{3n-3} dp_j dq_j, \tag{3.7}$$

where Q is given by (2.27). The integral in (3.7) is just the classical partition function of the system constrained to the surface $S(f,i)$; i.e.

$$Q^* = \int_{S(f,i)} e^{-E^*/kT} \prod_2^{3n-3} dp_j dq_j. \tag{3.8}$$

If we now "quantize" our system and let $Q^* = Q_q^* h^{3n-4}$ and $Q = Q_q h^{3n-3}$, equation (2.35) takes the familiar form

$$k^E = (kT/h) \cdot Q_q^*/Q_q \tag{3.9}$$

associated with the theory of absolute reaction rates.

As shown by Horiuti, the surface which minimizes the rate constant k^E must satisfy the variational equation

$$\delta Q^* = 0, \tag{3.10}$$

which leads immediately to the condition

$$(kT)^{-1}\partial E^*/\partial q_1 = \sum_2^{3n-3} \rho_j^{-1}, \tag{3.11}$$

where the ρ_j's are the principal radii of curvature of the surface $S(f,i)$. If $S(f,i)$ is a Cartesian plane, eqn. (3.11) becomes

$$\partial E^*/\partial q_1 = \partial V_0^*/\partial q_1 = 0,$$

which locates the surface at the saddle point, as in the Eyring theory. It is not clear, in general, how much the rate can be reduced by employing more complicated surfaces, but Horiuti has made estimates which indicate that, in cases where the barrier height is not large compared to kT, effects due to curvature could be significant.

C. Available Energy Theory

The available energy theory is based on the work of Lindemann[7] and Hinshelwood.[8] The basic assumption of this theory[9] is that a reaction can occur only for those collisions in which sufficient energy is "available" in some number, v, of quadratic terms in the energy of the reactants in the center-of-mass system. If all the terms in the energy are included, this certainly gives an upper limit to the reaction rate. The difficulty is that this usually leads to a gross overestimate of the rate, and v must be restricted to a smaller number. At this point the theory becomes reduced to a sort of guessing game, in which even for simple molecules it is possible to obtain results that vary by orders of magnitude depending on the choice of v. In spite of this objection, the theory is useful for correlating experimental data and setting limits for unknown rates of complex reactions.

The appropriate trial surface for this theory is defined by the constraints

$$S = r - a = 0 \tag{3.12}$$

and

$$p^2/2\mu + \sum_2^v \beta_j x_j^2 \geqslant D, \tag{3.13}$$

where a is an assumed collision diameter, r and p are the radial separation and conjugate momentum, μ is the reduced mass for the collision, x_j is a generalized coordinate, β_j is the coefficient of x_j^2 in the energy equation, and D is the energy required for a reaction. In addition to (3.12) and (3.13), we also have the energy equation

$$E = p^2/2\mu + \sum_{2}^{6n-7} \beta_j x_j^2. \tag{3.14}$$

Note that in (3.14) we have tacitly assumed that the interaction potential at $r = a$ may be neglected. With these constraints, the only non-vanishing Jacobian in (2.26) is $J_1 = \partial E/\partial p = \dot{r}$, and the available energy rate constant can be expressed

$$k_d^A = Q^{-1} \int e^{-E/kT} dE \prod_{2}^{6n-7} dx_j, \tag{3.15}$$

with

$$Q = V^{-1} \int e^{-E/kT} dp dr \prod_{2}^{3n-3} dp_j dq_j. \tag{3.16}$$

Expressions (3.15) and (3.16) can easily be integrated by using (3.12), (3.13), and (3.14), and this leads to the well-known result

$$k_d^A = \pi a^2 \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} \Gamma^{-1}\left(\frac{v+1}{2}\right) \int_{D/kT}^{\infty} e^{-x} x^{(v-1)/2} dx, \tag{3.17}$$

which for $kT/D \ll 1$ becomes approximately

$$k_d^A \approx \pi a^2 \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} \Gamma^{-1}\left(\frac{v+1}{2}\right)\left(\frac{D}{kT}\right)^{(v-1)/2} e^{-D/kT}, \tag{3.18}$$

where Γ is the Γ-function.

In concluding this Section, we note that the above calculation does not represent a rigorous application of the variational theory because the surface $r = a$ does not completely divide the reactants from the products unless the interaction potential is assumed to be sharply cut off at a. That is to say, our surface has "holes" in it through which the systems can "leak" without contributing to the integral in (3.15). We cannot claim, therefore, that (3.17) is a rigorous upper limit and vary our a to obtain a minimum rate. If we did we would, of course, get zero for an answer. A further criticism of (3.17) which becomes important at high temperatures

is that intergrals over the internal degrees of freedom of the reactants have all been extended to infinity, and no account is taken of the fact that finite potentials are involved.

D. Statistical Theory

In the opinion of the writer, the most serious criticism of the available energy theory as outlined above is that it fails to include explicitly a factor giving the reaction probability when the energy is available. This omission is responsible for many of the apparent difficulties and inconsistencies which arise in the practical application of the theory and, in 1958, led the writer to propose a statistical theory[10] of reaction rates in which the reaction probability was assumed to be proportional to the rate of flow of phase fluid across the boundaries of a collision complex into the product state. Before this, the same assumption was used by Hart, Gray, and Guier[11] in order to estimate branching ratios for atomic excitation by electron impact. Recently, a similar quantum-mechanical theory was proposed by Light,[12] that in its original form failed to satisfy detailed balancing and was subsequently revised by Pechukas and Light[13] to a form representing a special case of the writer's more general theory.[10]

Fundamentally, the statistical theory is based on scattering theory in the strong-coupling approximation,[14] and a derivation of the theory from first principles has been given by Eu and Ross.[15] It is also closely related to the compound nucleus theory of nuclear reactions[14] and Fermi's statistical theory of meson production.[16]

To obtain an expression for the statistical rate constant, we postulate the formation of a collision complex $\Omega(*)$ through which the reaction passes. Let $S(f,*)$ be that part of the surface of the collision complex through which the reaction products enter the final state f. Then the partial rate at which products are formed in this state with fixed total energy H, momentum $\mathbf{P}$, and angular momentum L, obtained from (2.18), is $\langle\rho\rangle_f\Gamma(f,*)$, and the probability of forming this state is exactly

$$P_f(H,\mathbf{P},L) = \langle\rho\rangle_f\Gamma(f,*)/\sum_j\langle\rho\rangle_j\Gamma(j,*). \tag{3.19}$$

Note that in writing (3.19), we have made the assumption that the reaction probability is independent of the position of the complex and the orientation of the total angular momentum.

The basic assumption of the statistical theory is that the mean value of the density $\langle\rho\rangle$ on the surface of the collision complex is the same for all product channels. With this assumption, (3.19) becomes

$$P_f(H,\mathbf{P},L) = \Gamma(f,*)/\sum_j \Gamma(j,*), \tag{3.20}$$

which is independent of the manner in which the collision complex was formed and depends only on the location of its boundaries and the Hamiltonian H determining the flow field of the phase fluid. The statistical rate constant may now be obtained by inserting (3.20) into (2.18), integrating over the ignorable coordinates $\mathbf{R}$, and substituting the result into (2.24). This gives the expression

$$k^S = \frac{V^v}{N(i)} \int_{S(*,i)} \langle\rho\rangle_i \frac{\Gamma(f,*)\Gamma(i,*)}{\sum_j \Gamma(j,*)}\, dH d\mathbf{P} dL d\omega_L dM d\phi_L, \tag{3.21}$$

which is equivalent to equation (5) of the writer's previous paper.[10]

We now consider the important special case in which the collisions are binary, and the boundary of the collision complex is defined by the equation

$$S = r - z(l) = 0, \tag{3.22}$$

where r and l are the radial separation and orbital angular momentum of the reactants, and $z(l)$ is the position of the maximum in the effective potential $V'(r)$ governing the radial motion of the reactants. We further assume that the interactions are negligible for $r > z$, so that the internal energy $E'(l',\boldsymbol{\alpha})$ and rotational angular momentum l' of the molecules are constants of the motion.

The Hamiltonian can then be written

$$H = P^2/2M + E'(l',\boldsymbol{\alpha}) + E_j, \tag{3.23}$$

where

$$E_j = p^2/2\mu_j + l^2/2\mu_j r^2 + V_j(r) \tag{3.24}$$

is the relative kinetic energy of the collision partners, p is the radial momentum conjugate to r, μ_j is the reduced mass for the collision, and $\boldsymbol{\alpha}$ stands for the set of action variables

$$\alpha_k = \oint p_k dq_k \tag{3.25}$$

required to complete the description of the reactants or products in the state j.

For the surface defined by (3.22) and the Hamiltonian (3.23), the only non-vanishing Jacobian in (2.19) and (2.20) is $J_1 = \partial H/\partial p = p/\mu$, and the mean density $\langle \rho \rangle_i$ and flow rate $\Gamma(j,*)$ in (3.21) can be written explicitly

$$\langle \rho \rangle_i = \Gamma^{-1}(i,*) \int_{S(i,*)} \rho dl d\omega dl' d\omega' \sum_1^{3n-8} d\alpha_k \tag{3.26}$$

and

$$\Gamma(j,*) = \int_{S(j,*)} dl d\omega dl' d\omega' \sum_1^{3n-8} d\alpha_k, \tag{3.27}$$

where ω and ω' are the Euler angles corresponding to rotation about l and l', and the surface $S(j,*)$ is defined by the set of constraints

$$r = z, \qquad p > 0, \qquad l + l' > L > |l - l'|. \tag{3.28}$$

Note that (3.26) and (3.27) contain implicitly the fact that the Jacobian of the transformation from m, ϕ, m', ϕ' to L, ω_L, M, ϕ_L is unity, where m and m' are the z-components of l and l', and ϕ and ϕ' are the corresponding Euler angles corresponding to rotation about the z-axis. We may also obtain an explicit expression for $N(i)$ from (2.4):

$$N(i) = V \int \rho d\mathbf{P} d\mathbf{p} d\mathbf{r} dl' d\omega' dm' d\phi' \sum_1^{3n-8} d\alpha_{ik}, \tag{3.29}$$

where we have integrated over $d\mathbf{R}$.

To compare these results directly with those of Pechukas and Light, we require the differential rate constant $k^s(H,E_i,l'_i,\boldsymbol{\alpha}_i,l'_f,\boldsymbol{\alpha}_f)$ for reactions having fixed total energy H and relative kinetic energy E_i in the initial state, and specified values of rotational angular momentum l' and action $\boldsymbol{\alpha}$ in the initial and final states. This is easily obtained from our integral expressions by simply deleting these variables, and we find, on combining (3.21), (3.26), (3.27), and (3.29) and integrating over angles,

$$k^S(H,E_i,l'_i,\boldsymbol{\alpha}_i,l'_f,\boldsymbol{\alpha}_f) = \frac{\pi v_i}{(2\mu_i E_i) 2l'_i} \int dL dM \frac{\gamma(f,*)\gamma(i,*)}{\Gamma(*)}, \tag{3.30}$$

where $v_i = (2E_i/\mu_i)^{\frac{1}{2}}$ is the relative velocity for the collision,

$$\gamma(j,*) = \int_{S(j,*)} dl \tag{3.31}$$

is the differential flow rate of phase fluid into the state j, and the surface $S(j,*)$ is defined by (3.28) together with (3.23) and (3.24).

To "quantize" the system, it is simply necessary to measure angular momentum in units of $\hbar$, action in units of h, and convert integrals to sums. Thus (3.30) becomes

$$k^s(H,E_i,l_i',\alpha_i,l_f',\alpha_f) = \frac{\pi\hbar^2 v_i}{(2\mu_i E_i)(2l_i'+1)} \cdot \sum_{L,M} \frac{\gamma(f,*)\gamma(i,*)}{\Gamma(*)} \tag{3.32}$$

where

$$\gamma(j,*) = \sum_l X_l(L,E_j,l_j'), \tag{3.33}$$

$$\Gamma(*) = \sum_{l_f',\alpha_f} \gamma(f,*), \tag{3.34}$$

and the characteristic function X_l determined by the constraints (3.28), (3.23), and (3.24) is

$$X_l = \begin{cases} 1 : l + l_j' \geqslant L \geqslant |l - l_j'|, \quad E_j \geqslant V_j'(z) \\ 0 : \text{ otherwise} \end{cases} \tag{3.35}$$

Since the cross section σ for a reaction is simply k/v, eqn. (3.32) is identical with eqn. (7) of Pechukas and Light.[13]

It is interesting (and comforting) to note that while the results obtained by the writer and Pechukas and Light are the same, the methods used to arrive at them could hardly be more different. Pechukas and Light start with a quantum-mechanical formulation and introduce an arbitrary "measure," the character of which is then determined by detailed balancing arguments. This leaves the physical interpretation of the "measure" somewhat obscure. On the other hand, the writer starts with a classical approach and immediately identifies the "measure" as the rate of flow of phase fluid into the various states. This gives a clear physical meaning to the theory. In this connection it may be observed that it was the omission of the flow velocity which led to the detailed balancing failure found in Light's original paper.[12] The same error was also made by Horie and Kasuga.[17]

The conditions under which the statistical theory may actually be valid in chemical reactions are not yet clear. In the writer's work on three-body atom recombination,[10] it has been found unsatisfactory. On the other hand, Pechukas and Light have reported some success in applying the theory to exchange reactions involving ionic molecules. There is also the possibility that the theory may be a reasonable approximation for reactions involving polyatomic molecules. In any case, the theory is an improvement over the available energy theory if only because it satisfies detailed balancing.

IV. THREE-BODY RECOMBINATION AND DISSOCIATION

One of the most important applications of the variational theory which has been made to date is to the problem of three-body recombination and dissociation of atoms and ions. This problem has been treated by a variety of methods, and we shall review several of them to illustrate how the calculations are made and to permit a comparison of the results. For the sake of uniformity and to remove the strong dependence on the Boltzmann factor, we shall give our results in terms of three-body recombination rate constants. The four rate constants that we shall consider in detail are the (1) available energy, (2) three-body collision, (3) Wigner, and (4) barrier-rate constants. We shall omit detailed consideration of the statistical rate constant[10] because the calculations are rather complicated, and the theory is asymptotic to the available energy and three-body collision theories at high and low temperatures, respectively, and varies smoothly in between.

A. The Model

All of our calculations will be made for a system of three distinguishable particles. We assume that the motion can be described classically and that the full three-body interaction potential V_0 is known. We further assume in the case of atoms and molecules that electronic transitions do not occur during a collision, so that V_0 is invariant. The canonical coordinates p_{12}, r_{12}, l_{12}, ω_{12}, m_{12}, ϕ_{12} will be used to describe the relative motion of particles 1 and 2 and the coordinates p_3, r_3, l_3, ω_3, m_3, ϕ_3 to describe the motion of

particle 3 with respect to the center-of-mass of the "molecule" composed of particles 1 and 2. In this set p and r denote the radial momentum and separation, l and ω the angular momentum and conjugate Euler angle, and m and ϕ the z-component of l and conjugate Euler angle. These coordinates, which are shown in Fig. 1, are closely related to the Delaunay elements[18] used in astronomy and in the old Bohr quantum theory.

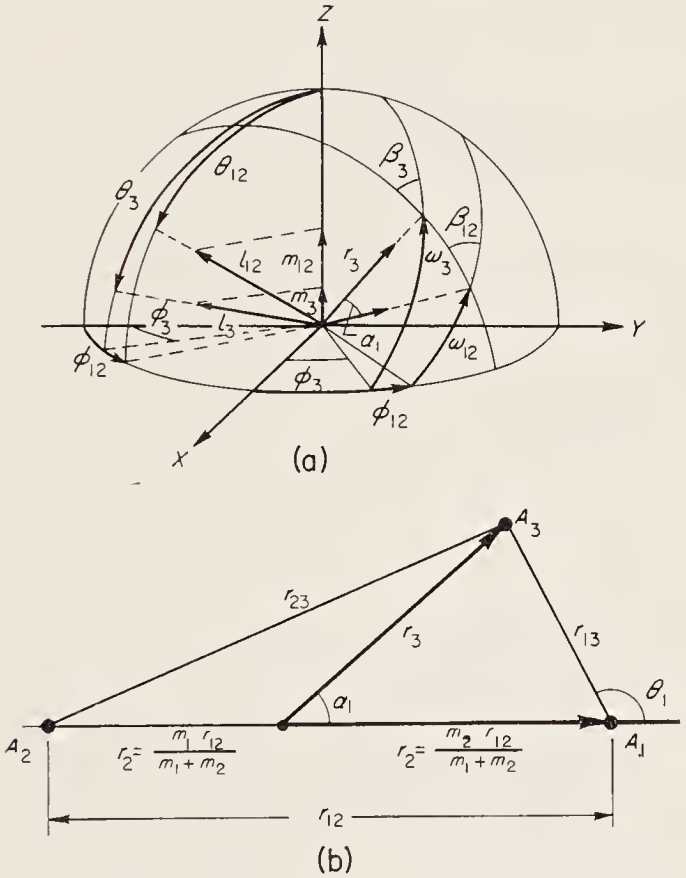

Fig. 1. Coordinates used to describe the relative motion of three particles.

The Hamiltonian in the center-of-mass system can now be written

$$E = E_{12} + p_3^2/2\mu_3 + l_3^2/2\mu_3 r_3^2 + V_3, \tag{4.1}$$

where

$$E_{12} = p_{12}^2/2\mu_{12} + l_{12}^2/2\mu_{12} r_{12}^2 + V_{12} \tag{4.2}$$

is the energy of the molecule,

$$V_3 = V_0 - V_{12} \tag{4.3}$$

is the interaction potential, μ_3 is the reduced mass for the collision, and V_{12} and μ_{12} are the interaction potential and reduced mass for the molecule.

To describe an attractive interaction between atoms, we shall use the Morse potential

$$V_M(r) = D[(1 - e^{-\beta(r-r_e)})^2 - 1]. \tag{4.4}$$

The corresponding "effective potential" governing the radial motion of the molecule is

$$V'(r) = l^2/2\mu r^2 + V_M(r). \tag{4.5}$$

The general characteristics of the "effective potential" for a sharply cut-off interaction such as the Morse interaction are shown

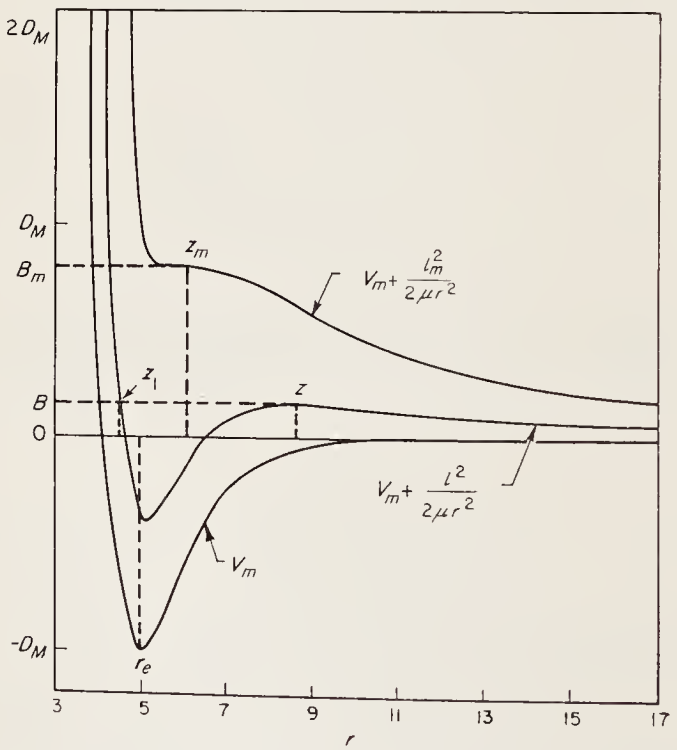

Fig. 2. General characteristics of the effective potential for a Morse interaction.

by the curves in Fig. 2. If l is not too large, there is a relative maximum, the rotational barrier, at a radius z given by

$$(dV'/dr)_z = (dV_M/dr - l^2/\mu r^3)_z = 0. \tag{4.6}$$

If we let B denote the height of the rotational maximum, then it can easily be shown, by using (4.5) and (4.6), that

$$dB/dl^2 = (2\mu z^2)^{-1}. \tag{4.7}$$

This equation has been found very useful in dealing with collision problems.

As in our previous calculations, we shall assume that the internal state of the system can be described by a Boltzmann distribution $\rho = \rho_0 \exp(-E/kT)$ and compute equilibrium rate constants.

B. Available Energy Rate

We shall first calculate a rate constant for atomic recombination based on the available-energy theory described in Section III C. However, in our present calculation, we shall use a somewhat more realistic trial surface which takes into account the finite depth of the Morse potential. This surface $S(A)$ is defined by

$$S = r_3 - a = 0, \tag{4.8}$$

where a is a characteristic collision diameter that may be taken roughly as the radius at which the magnitude of the interaction potential V_3 in (4.1) is equal to kT. In addition we require that the molecule be bound in the initial state, so that

$$E_{12} \leqslant B \leqslant B_m, \qquad r_{12} \leqslant z, \tag{4.9}$$

where B_m is the maximum value of B; we require further that the energy to dissociate be available, so that

$$E \geqslant 0. \tag{4.10}$$

The equilibrium rate constant for this surface can now be obtained from (2.26) and after integration over angles can be written

$$k_r^A = f(2\pi)^4 Q^{-1} \int_{S(A)} e^{-E/kT} \tau_{12} dE_{12} dl_1^2 dl_{12}^2 dE, \tag{4.11}$$

where

$$f = g_{12}/g_1 g_2 \tag{4.12}$$

is the electronic degeneracy factor (2.21),

$$Q = (2\pi\mu_{12}kT)^{3/2}(2\pi\mu_3 kT)^{3/2}, \tag{4.13}$$

and the period τ_{12} for a rotating Morse oscillator can be approximated

$$\tau_{12} \approx [2\pi^2\mu_{12}/\beta^2(B - E_{12})]^{\frac{1}{2}}. \tag{4.14}$$

The major contribution to the integral in (4.11) comes from the region of phase space in the vicinity of the minimum in the Morse potential, and a very satisfactory approximation to (4.11) can be obtained by setting r_{12} in (4.2) equal to r_e. This gives

$$k_r^A = f\pi a^2\left(\frac{4\pi r_e^2}{\beta}\right)\left(\frac{2D}{\mu_3}\right)^{\frac{1}{2}} \cdot \frac{8}{15} \cdot \frac{D}{kT}\left(\frac{D}{kT} + 5\right). \tag{4.15}$$

This expression for the available energy recombination rate constant is valid for all values of kT/D and is not restricted to $kT/D \ll 1$ as is the conventional available-energy recombination rate constant obtained by detailed balancing from (3.17). A plot of k_r^A as a function of kT is shown in Fig. 3.

C. Three-body Collision Rate

Although a three-body collision may occur in several ways, for our present purpose we shall define it as a collision of particle 3 with a pair of free particles 1 and 2 orbiting at a separation r_{12} less than the radius of the rotational maximum z. The corresponding trial surface $S(T)$ is determined by the constraints

$$S = r_3 - a = 0, \qquad r_{12} \leqslant z, \qquad E_{12} \geqslant B \tag{4.16}$$

with the auxiliary conditions

$$E \geqslant 0, \qquad B \leqslant B_m, \tag{4.17}$$

and the three-body recombination rate constant obtained from (2.26) after integrating over angles is

$$k_r^T = f(2\pi)^4(2\mu_3 Q)^{-1}\int_{S(T)} e^{-E/kT}\tau_{12}dE_{12}dl_{12}^2dl_3^2dp_3^2, \tag{4.18}$$

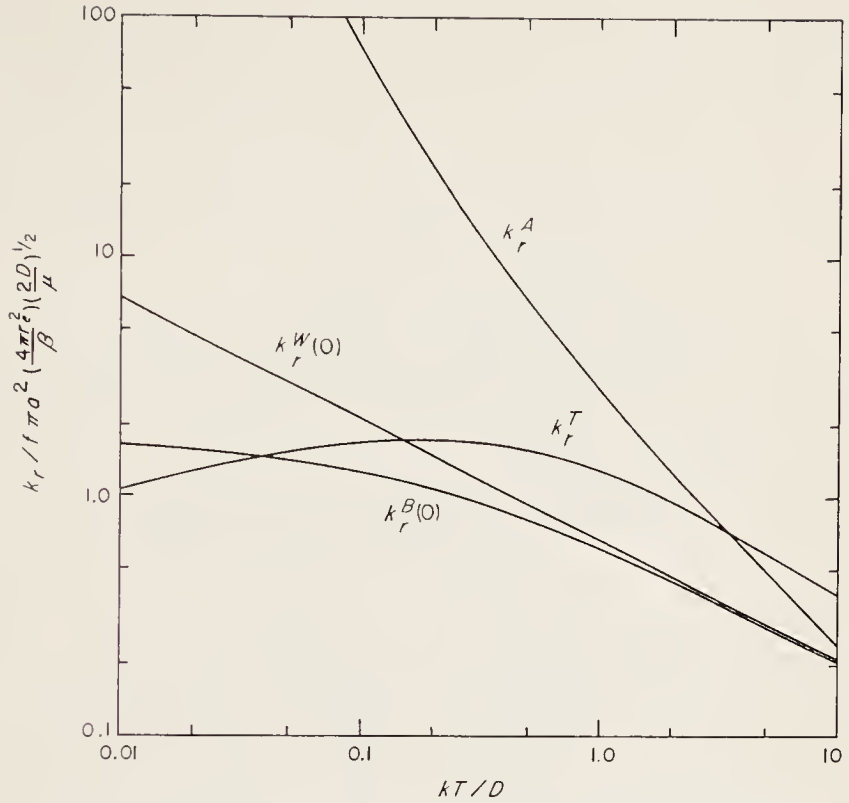

Fig. 3. Dimensionless comparisons of available energy k_r^A, three-body collision k_r^T, Wigner $k_r^W(0)$, and barrier $k_r^B(0)$ recombination rate constants for a Morse potential with $\beta r_e = 3$. Note that k_r^A and k_r^T scale as $\mu_3^{-\frac{1}{2}}$, while $k_r^W(0)$ and $k_r^B(0)$ scale as $\mu_{12}^{-\frac{1}{2}}$. See text for definition of parameters.

where Q is given by (4.13) and the effective collision time τ_{12} can be approximated

$$\tau_{12} = [2\mu_{12}/\beta^2(E_{12} - B)]^{\frac{1}{2}}. \tag{4.19}$$

The integration of (4.18) with respect to dl_3^2, dp_3^2, and dE_{12} can be carried out exactly and yields

$$k_r^T = \frac{f(2\pi a)^2}{\beta\mu_{12}} \left(\frac{2}{\pi\mu_3 kT}\right)^{\frac{1}{2}} \int e^{-B/kT} dl_{12}^2. \tag{4.20}$$

To carry out the remaining integration, we substitute the variable z for l_{12} using (4.7), so that (4.20) becomes

$$k_r^T = \frac{f(2\pi a)^2}{\beta} \left(\frac{8}{\pi\mu_3 kT}\right)^{\frac{1}{2}} \int e^{-B/kT} z^2 \frac{dB}{dz}\, dz. \tag{4.21}$$

We now observe that, for sharply cut-off potentials such as the Morse potential, the factor $(dB/dz)\exp(-B/kT)$ in the integrand of (4.21) has a strong maximum at the position z_2, defined by

$$(d/dz)[(dB/dz)\exp(-B/kT)]_{z_2} = 0. \tag{4.22}$$

Setting $z^2 = z_2^2$ in the integrand of (4.21), the remaining integration can be carried over dB and gives

$$k_r^I = f\pi a^2 \left(\frac{4\pi z_2^2}{\beta}\right)\left(\frac{2D}{\mu_3}\right)^{\frac{1}{2}} \frac{2}{\sqrt{\pi}} \left(\frac{kT}{D}\right)^{\frac{1}{2}} (1 - e^{-B_m/kT}). \tag{4.23}$$

It may be noted that this expression for the three-body collision rate constant is substantially identical to that obtained from Rice's theory[19] of dissociation by detailed balancing.

A plot of the three-body collision rate constant is shown in Fig. 3, and it is seen to be smaller than the available-energy rate constant for all values of $kT/D < 3$. Thus the available-energy rate constant cannot be regarded as a good approximation in this range in spite of the appealing fact that it gives a negative temperature coefficient more nearly in agreement with experiments.

For $kT/D > 3$, however, the available-energy theory does give a lower limit than the three-body collision theory. The physical reason for this is that, for small values of kT/D, the phase space available to three free particles is much smaller than that available to two, so that decay of the collision complex into three particles becomes the rate-limiting step. For large kT/D the reverse is true, and two-particle decay is the rate-limiting step. The statistical theory[10] of reaction rates automatically takes this into account and, as already mentioned, provides a smooth transition between the two expressions (4.15) and (4.23). It should be noted that, strictly speaking, neither of these expressions is a rigorous upper limit to the true rate constant because the trial surfaces used are "leaky". Nevertheless, they are sufficiently good for practical purposes, and the smaller of the two should give the best approximation to the true rate constant.

D. Wigner Rate

Wigner[2] obtained a rigorous upper limit to the three-body recombination rate constant by calculating the flow of molecules through the surface $E_{12} = 0$. This is the first of the surfaces

considered that divides molecules from free atoms without "leaks". It is also the first to depend on the momentum coordinates and, therefore, to involve explicitly the form of the interaction potential V_3.

In our present calculation we shall use a slightly more general trial surface $S(W)$ defined by

$$S = E_{12} + E_0 = 0, \qquad E \geqslant -E_0, \tag{4.24}$$

where E_0 is a constant that we shall later vary to obtain the minimum rate. For this surface there are two non-vanishing Jacobians in our general expression (2.26) for the rate constant. These are

$$J_1 = \frac{\partial E}{\partial p_{12}} \cdot \frac{\partial E_{12}}{\partial r_{12}} - \frac{\partial E}{\partial r_{12}} \cdot \frac{\partial E_{12}}{\partial p_{12}} = -\frac{p_{12}}{\mu_{12}} \cdot \frac{\partial V_3}{\partial r_{12}} \tag{4.25a}$$

and

$$J_2 = -\frac{\partial E}{\partial \omega_{12}} \cdot \frac{\partial E_{12}}{\partial l_{12}} = -\frac{l_{12}}{\mu_{12} r_{12}^2} \cdot \frac{\partial V_3}{\partial \omega_{12}} \tag{4.25b}$$

Substituting (4.25) into (2.26) we obtain

$$k_r^W(E_0) = fQ^{-1} \int_{S(W)} e^{-E/kT} \left(\frac{p_{12}}{|p_{12}|} \frac{\partial V_3}{\partial r_{12}} + \frac{\gamma_W}{r_{12}} \frac{\partial V_3}{\partial \omega_{12}} \right) \times dr_{12} dl_{12} d\omega_{12} dm_{12} d\phi_{12} dp_3 dr_3 dl_3 d\omega_3 dm_3 d\phi_3 \tag{4.26}$$

where

$$\gamma_W = r_{12} \frac{\partial p_{12}}{\partial l_{12}} = [2\mu_{12} r_{12}^2 (-E_0 - V_{12})/l_{12}^2 - 1]^{-\frac{1}{2}} \tag{4.27}$$

and Q is given by (4.13).

To integrate (4.26), it is convenient to make the transformation

$$d\omega_{12} dm_{12} d\phi_{12} = l_{12} d\beta_{12} d\beta_3 d \cos \alpha, \tag{4.28}$$

where β_{12}, β_3, and α are the angles shown in Fig. 1 which determine the relative position and velocities of the particles. Equation (4.26) can then be written

$$k_r^W(E_0) = fQ^{-1} \int_{S(W)} e^{-E/kT} \left(\frac{p_{12}}{|p_{12}|} \cdot \frac{\partial V_3}{\partial r_{12}} - \frac{\gamma_W \cos \beta_{12}}{r_{12}} \cdot \frac{\partial V_3}{\partial \alpha} \right) l_{12} \times dp_3 dl_3 d\omega_3 dm_3 d\phi_3 d\beta_3 d\beta_{12} dl_{12} dr_{12} dr_3 d \cos \alpha \tag{4.29}$$

and the integration over the first eight variables can be carried out conveniently in the order given. This yields

$$k_r^W(E_0) = \frac{f8\pi}{(kT)^2}\left(\frac{2kT}{\mu_{12}}\right)^{\frac{1}{2}}\int_{-E_0 > V_{12}} e^{(E_0 - V_3)/kT}\left[\left(\frac{\partial V_3}{\partial r_{12}}\right)^2 + \left(\frac{1}{r_{12}}\frac{\partial V_3}{\partial \alpha}\right)^2\right]^{\frac{1}{2}}$$
$$\times \Gamma\left(\frac{3}{2}, \frac{|V_3| - V_3}{2kT}\right)(-E_0 - V_{12})r_{12}^2 dr_{12} r_3^2 dr_3 d\cos\alpha, \quad (4.30)$$

where

$$\Gamma(n+1, x) = \int_x^\infty y^n e^{-y} dy \quad (4.31)$$

is the incomplete Γ-function.

The expression in square brackets in (4.30) can be recognized as the magnitude of the force acting to change the energy of the molecule. The two terms correspond to vibrational and rotational transitions, and we note that, if the interaction potential V_3 is assumed to be spherically symmetric, there will be no contribution due to rotational transitions.

1. *Atomic recombination.* To proceed further we must specify the interaction potential V_3. For the case of atomic recombination, we assume as a first approximation

$$V_3 \approx V_{13}(r_{13}) + V_{23}(r_{23}) \geqslant 0 \quad (4.32)$$

and observe that, if V_{13} and V_{23} are sufficiently steep, the integrand in (4.30) will possess a strong maximum on two spherical shells with radii a_{13} and a_{23} defined by

$$(d/dr_{13})[(dV_{13}/dr_{13})\exp(-V_{13}/kT]_{a_{13}} = 0 \quad (4.33a)$$

and

$$(d/dr_{23})[(dV_{23}/dr_{23})\exp(-V_{23}/kT]_{a_{23}} = 0. \quad (4.33b)$$

This "dumbbell model" permits one to divide the integral in (4.30) into two parts corresponding to integration over the two ends of the dumbbell, so that

$$k_r^W(E_0) = k_{r1}^W(E_0) + k_{r2}^W(E_0), \quad (4.34)$$

where

$$k_{r1}^W(E_0) = \frac{f8\pi}{(kT)^2}\left(\frac{\pi kT}{2\mu_{12}}\right)^{\frac{1}{2}}\left(\frac{m_2}{m_1 + m_2}\right)\int_{-E_0 > V_{12}, \theta_{1m} > \theta_1}(-E_0 - V_{12})$$
$$\times \frac{dV_{13}}{dr_{13}} e^{(E_0 - V_{13})/kT} r_{12}^2 dr_{12} r_{13}^2 dr_{13} d\cos\theta_1, \quad (4.35)$$

and we have made the transformation

$$r_3^2 dr_3 d\cos\alpha = r_{13}^2 dr_{13} d\cos\theta_1. \tag{4.36}$$

The angle θ_1 is shown in Fig. 1(b), and θ_{1m} is defined by

$$\cos\theta_{1m} = (a_{23}^2 - a_{13}^2 - r_{12}^2)/2a_{13}r_{12}. \tag{4.37}$$

$k_{r2}^W(E_0)$ is given by the corresponding expressions with the subscripts 1 and 2 interchanged.

The integration over $dr_{13}d\cos\theta_1$ may now be carried out approximately by setting $r_{13}^2 = a_{13}^2$ in the integrand of (4.35), and we find

$$k_r^W(E_0) = f4\pi\left(\frac{2\pi\mu_{12}}{kT}\right)^{\frac{1}{2}} e^{E_0/kT}\int_{-E_0>V_{12}}(-E_0 - V_{12})r_{12}^2 \times [a_{13}^2 m_1^{-1}(1-\cos\theta_{1m}) + a_{23}^2 m_2^{-1}(1-\cos\theta_{2m})]dr_{12}, \tag{4.38}$$

where we have added $k_{r1}^W(E_0)$ and $k_{r2}^W(E_0)$. This is equivalent to the result obtained by Wigner.[2]

The remaining integration over dr_{12} may also be carried out approximately by observing that for a Morse potential (4.4) the factor $(-E_0 - V_{12})$ has a strong maximum at $r_{12} = r_e$. Expanding the integrand about this point, we obtain

$$k_r^W(E_0) = f\pi a^2\left(\frac{4\pi r_e^2}{\beta}\right)\left(\frac{2D}{\mu_{12}}\right)^{\frac{1}{2}}\frac{4}{3\sqrt{\pi}}\left(\frac{D}{kT}\right)^{\frac{1}{2}}\left(1-\frac{D}{E_0}\right)^{3/2} e^{E_0/kT}, \tag{4.39}$$

where

$$a^2 = \frac{m_2 a_{13}[(a_{13}+r_e)^2 - a_{23}^2] + m_1 a_{23}[(a_{23}+r_e)^2 - a_{13}]}{2(m_1+m_2)r_e} \tag{4.40}$$

is the square of an effective collision radius.

For $E_0 \ll D$, $k_r^W(E_0)$ is an increasing function of E_0, and since E_0 must be greater than zero to avoid a "hole" in the trial surface, the best choice of E_0 is the one made by Wigner, namely, zero, and (4.39) becomes simply

$$k_r^W(0) = f\pi a^2\left(\frac{4\pi r_e^2}{\beta}\right)\left(\frac{2D}{\mu_{12}}\right)^{\frac{1}{2}}\frac{4}{3\sqrt{\pi}}\left(\frac{D}{kT}\right)^{\frac{1}{2}}. \tag{4.41}$$

A plot of this expression is shown in Fig. 3. For $\mu_{12} \sim \mu_3$, the Wigner rate is smaller than the available energy rate over the entire temperature range shown and smaller than the three-body

collision rate for $kT/D \gtrsim .15$. For light third bodies, i.e., $\mu_3 \ll \mu_{12}$, the Wigner rate will be the best approximation to somewhat lower temperature, but the three-body collision rate will still give the smallest limit over most of the range $kT/D < 0{\cdot}1$ where experiments have been performed.

2. *Electron recombination.* A calculation similar to that described above has also been made by Makin and Keck[20] for the three-body electron recombination process $A^+ + e + e \rightarrow A + e$. In this case the integral in (4.29) diverges linearly with r_3 owing to the long range of the Coulomb forces involved, and a cut-off must be introduced. Since the energy transfer is, in general, small for collisions in which the product of the angular frequency ω of an oscillator and the collision time τ is large, a reasonable cut-off is $\omega\tau = 1$. The integration of (4.29) may then be carried out with the aid of a computer and the results represented by an expression of the form

$$k_r^e(E_0) = \frac{3\pi}{4}\left(\frac{e}{kT}\right)^5\left(\frac{8kT}{\pi m_e}\right)^{\frac{1}{2}}\left(\frac{kT}{E_0}\right)^4 (e^{8E_0/5kT} + 5e^{E_0/kT}). \qquad (4.42)$$

This rate constant has a minimum at $E_0/kT = 5/2$, which may be interpreted physically as giving the location of the rate-limiting step or "bottleneck" in the electron cascade toward the ground state. Similar theoretical results have been obtained by Bates, Kingston, and McWhirter,[21] and supporting experimental evidence is provided by the work of Hinnov and Hirshberg.[22]

E. Barrier Rate Constant

The barrier rate constant was introduced by the writer[4] to take into account the effects of the rotational barrier. It involves passage of a molecule through a trial surface a fixed energy E_0 below the top of the rotational barrier. This surface $S(B)$ is defined by the constraints

$$S = E_{12} - B_{12} + E_0 = 0, \qquad E \geqslant -E_0, \qquad (4.43)$$

and gives two non-vanishing Jacobians in (2.26), namely:

$$J_1 = \frac{\partial E}{\partial p_{12}} \cdot \frac{\partial E_{12}}{\partial r_{12}} - \frac{\partial E_{12}}{\partial p_{12}} = -\frac{p_{12}}{\mu_{12}} \cdot \frac{\partial V_3}{\partial r_{12}} \qquad (4.44a)$$

and

$$J_2 = -\frac{\partial E}{\partial \omega_{12}} \cdot \frac{\partial (E_{12} - B)}{\partial l_{12}} = -\left(\frac{l_{12}}{\mu_{12} r_{12}^2} - \frac{dB}{dl_{12}}\right) \frac{\partial V_3}{\partial \omega_{12}}. \quad (4.44b)$$

Substituting (4.44) into (2.26) and making the transformation (4.28) discussed in Section IV D, we obtain the expression

$$k_r^B(E_0) = fQ^{-1} \int_{S(B)} e^{-E/kT} \left(\frac{p_{12}}{|p_{12}|} \frac{\partial V_3}{\partial r_{12}} - \frac{\gamma_B \cos \beta_{12}}{r_{12}} \cdot \frac{\partial V_3}{\partial \alpha}\right) l_{12} \times dp_3 dl_3 d\omega_3 dm_3 d\phi_3 d\beta_3 d\beta_{12} dl_{12} dr_{12} dr_3 d \cos \alpha, \quad (4.45)$$

where

$$\gamma_B(r_{12}, l_{12}, E_0) = \frac{(1 - 2\mu_{12} r_{12}^2 dB/dl_{12}^2)}{[2\mu_{12} r_{12}^2 (B - E_0 - V_{12})/l_{12}^2 - 1]^{\frac{1}{2}}}, \quad (4.46)$$

which is identical in form to (4.29).

Following Woznick,[23] we integrate (4.45) exactly over the first seven variables, obtaining

$$k_r^B(E_0) = f4 \left(\frac{2kT}{\mu_{12}}\right)^{\frac{1}{2}} \int_{\gamma_B > 0} e^{\varepsilon - b - u} \Gamma\left(\frac{3}{2}, \frac{|b + u| - (b + u)}{2}\right) \times F z^2 r_3^2 \frac{db}{dz} \left|\frac{\partial u}{\partial r_3}\right| dz dr_{12} dr_3 d \cos \alpha, \quad (4.47)$$

where $\varepsilon = E_0/kT$, $b = B/kT$, $u = V_3/kT$,

$$F(r_{12}, \alpha, r_3, z, E_0) = 4\left(\eta \frac{\partial r_3}{\partial r_{12}} + \frac{\gamma_B \cos \eta}{r_{12}} \frac{\partial r_3}{\partial \alpha}\right), \quad (4.48)$$

$$\gamma_B(r_{12}, z, E_0) = \left[1 - \left(\frac{r_{12}}{z}\right)^2\right] \left[\left(\frac{r_{12}}{z}\right)^2 \frac{B - E_0 - V_{12}(r_{12})}{B - V_{12}(z)} - 1\right]^{-\frac{1}{2}}, \quad (4.49)$$

and

$$\eta = \begin{cases} \sin^{-1} \left|\dfrac{r_{12}}{\gamma_B} \dfrac{\partial \alpha}{\partial r_{12}}\right| & : \quad \left|\dfrac{r_{12}}{\gamma_B} \dfrac{\partial \alpha}{\partial r_{12}}\right| \leqslant 1 \\ \dfrac{\pi}{2} & : \quad \left|\dfrac{r_{12}}{\gamma_B} \dfrac{\partial \alpha}{\partial r_{12}}\right| > 1 \end{cases} \quad (4.50)$$

Note that we have transformed from dl_{12} to dz by using (4.7).

We now assume, for simplicity, that $\partial u/\partial r_3$ has only one zero, corresponding to a single minimum in the interaction potential of depth $u_m(\alpha,r_{12})$ at a radius $r_{3m}(\alpha,r_{12})$. Under these conditions, the factor

$$e^{-b-u}\Gamma\left(\frac{3}{2}, \frac{|b+u| - (b+u)}{2}\right)\frac{db}{dz}\left|\frac{\partial u}{\partial r_3}\right|$$

in the integrand of (4.47) will have relatively strong maxima at the points (z_2,a_+) and (z_2,a_-) in the (z,r) plane defined by

$$\frac{\partial}{\partial z}\left[e^{-b}\Gamma\left(\frac{3}{2}, \frac{|b+u| - (b+u)}{2}\right)\frac{db}{dz}\right]_{z_2,a_\pm} = 0$$

and (4.51)

$$\frac{\partial}{\partial r_3}\left[e^{-u}\Gamma\left(\frac{3}{2}, \frac{|b+u| - (b+u)}{2}\right)\left|\frac{\partial u}{\partial r_3}\right|\right]_{z_2,a_\pm} = 0,$$

where $a_+(\alpha,r_{12}) > r_{3m}(\alpha,r_{12}) > a_-(\alpha,r_{12})$. If we further assume that the remaining factor $Fz^2r_3^2$ varies relatively slowly, we may evaluate it at the points (z_2,a_+) and $z_2,a_-)$ and express (4.47) in the form

$$k_r^B(E_0) = f\pi z_2^2\left(\frac{8kT}{\pi\mu_{12}}\right)^{\frac{1}{2}}[\Omega_+(E_0) + \Omega_-(E_0)](1 - e^{-b_m(E_0)})e^{\epsilon}, \quad (4.52)$$

where

$$\Omega_\pm(E_0) = \int_{\gamma_B>0} F(r_{12},\alpha,a_\pm,z_2,E_0)G_\pm a_\pm^2 d\cos\alpha dr_{12}, \quad (4.53)$$

$G_-(E_0) =$

$$\frac{2}{\sqrt{\pi}}(1 - e^{-b_m(E_0)})^{-1}\int_{-u_m}^{\infty} du\int_0^{b_m(E_0)} db e^{-b-u}\Gamma\left(\frac{3}{2}, \frac{|b+u| - (b+u)}{2}\right)$$

$$= e^{u_m}[\Gamma(\tfrac{7}{2},u_m)\Gamma^{-1}(\tfrac{7}{2}) - e^{-b_m(E_0)}]/(1 - e^{-b_m(E_0)}), \quad (4.54a)$$

and

$G_+(E_0) =$

$$\frac{2}{\sqrt{\pi}}(1 - e^{-b\Gamma(E_0)})^{-1}\int_{-u_m}^{0} du\int_0^{b_m(E_0)} db e^{-b-u}\Gamma\left(\frac{3}{2}, \frac{|b+u| - (b+u)}{2}\right)$$

$$= G_-(E_0) - 1. \quad (4.54b)$$

In (4.54), $b_m(E_0)$ is the dimensionless height of the rotational barrier for which E_0 is just equal to the depth of the minimum in the effective potential curve, and we have tacitly assumed that

$b_m(E_0) \gtrsim u_m$. Note that $\Omega_\pm(E_0)$ is an effective interaction volume of molecular size.

Equation (4.52) is the general expression for the barrier rate constant. It is valid for all interaction potentials having at most a single minimum and sufficiently sharply cut-off to make the integrals convergent.

To proceed further we must now specify the nature of the interaction potential.

Dumbbell model. The only detailed calculations of the barrier rate constant (4.52) which have been made to date use the "dumbbell" model $V_3 = V_{13}(r_{13}) + V_{23}(r_{23})$ and are restricted to the case where the attractive minima in $V_{13}(r_{13})$ and $V_{23}(r_{23})$ are not deep compared to kT. As discussed in the preceding Section, the integral in (4.53) can then be expressed as a sum of contributions from the two ends of the "dumbbell"

$$\Omega_\pm(E_0) = 4\pi[z_2(E_0) - z_1(E_0)][a^2_{13\pm}(E_0) + a^2_{23\pm}(E_0)], \quad (4.55)$$

where $z_1(E_0)$ and $z_2(E_0)$ are, respectively, the inner and the outer turning point for a Morse oscillator with an energy $E_{12} = B - E_0$ and a rotational maximum at $z_2 \equiv z_2(0)$. $a_{1\pm}(E_0)$ and $a_{2\pm}(E_0)$ are effective radii given by

$$a^2_{j\pm}(E_0) = \mu_{12} m_j^{-1} a^2_{j3\pm} \phi_{j\pm}(E_0) G_{j\pm}(E_0), \qquad j = 1,2 \qquad (4.56)$$

for collisions with the two ends of the dumbbell. The factor $\phi_{j\pm}(E_0)$ in (4.56) is a slowly decreasing function of E_0, which must be calculated numerically and for most molecules of interest is approximately 1/3. It is defined by the equation

$$\phi_{j\pm}(E_0) = \tfrac{1}{4}[z_2(E_0) - z_1(E_0)]^{-1} \int_{z_1}^{z_2} H(\theta_{jm\pm}, \gamma_B) dr_{12},$$

where

$$H(\theta,\gamma_B) = \begin{cases} (1+\gamma_B^2)^{\frac{1}{2}} \left(1 - \dfrac{\cos\theta}{|\cos\theta|}\right) + \dfrac{\cos\theta}{|\cos\theta|} \sin^2\theta : \cot^2\theta \geqslant \gamma_B^2 \\ \dfrac{2}{\pi}\left\{(1+\gamma_B^2)^{\frac{1}{2}} \tan^{-1} \dfrac{(\gamma_B^2 - \cot^2\theta)^{\frac{1}{2}}}{(1+\gamma_B^2)^{\frac{1}{2}} \cot\theta} + \right. \\ \left. \left[\sin^{-1} \dfrac{\cot\theta}{\gamma_B} - (\gamma_B^2 - \cot^2\theta)^{\frac{1}{2}} \cot\theta\right] \sin^2\theta\right\} : \cot^2\theta \leqslant \gamma_B^2, \end{cases} \quad (4.58)$$

and θ_{jm} and γ_B are given by (4.37) and (4.49) with $z = z_2$. For $\theta \approx \pi/2$, $H \approx (1 + \gamma_B^2)^{\frac{1}{2}}$.

Combining (4.52), (4.55), and (4.56), we obtain the barrier rate constant in the form

$$k_r^B(E_0) = f\pi a^2(E_0)(4\pi z_2^2)\,[z_2(E_0) - z_1(E_0)]\left(\frac{8kT}{\pi\mu_{12}}\right)^{\frac{1}{2}}(1 - e^{-b_m(E_0)})e^{\varepsilon}, \tag{4.59}$$

where

$$a^2(E_0) = \mu_{12}\left[\left(\frac{a_{13-}^2}{m_1}\phi_{1-}G_{1-} + \frac{a_{23-}^2}{m_2}\phi_{2-}G_{2-}\right) + \left(\frac{a_{13+}^2}{m_1}\phi_{1+}G_{1+} + \frac{a_{23+}^2}{m_2}\phi_{2+}G_{2+}\right)\right] \tag{4.60}$$

is the square of the effective collision radius.

The functions necessary to compute $k_r^B(E_0)$ for homonuclear molecules interacting with repulsive or only weakly attracting

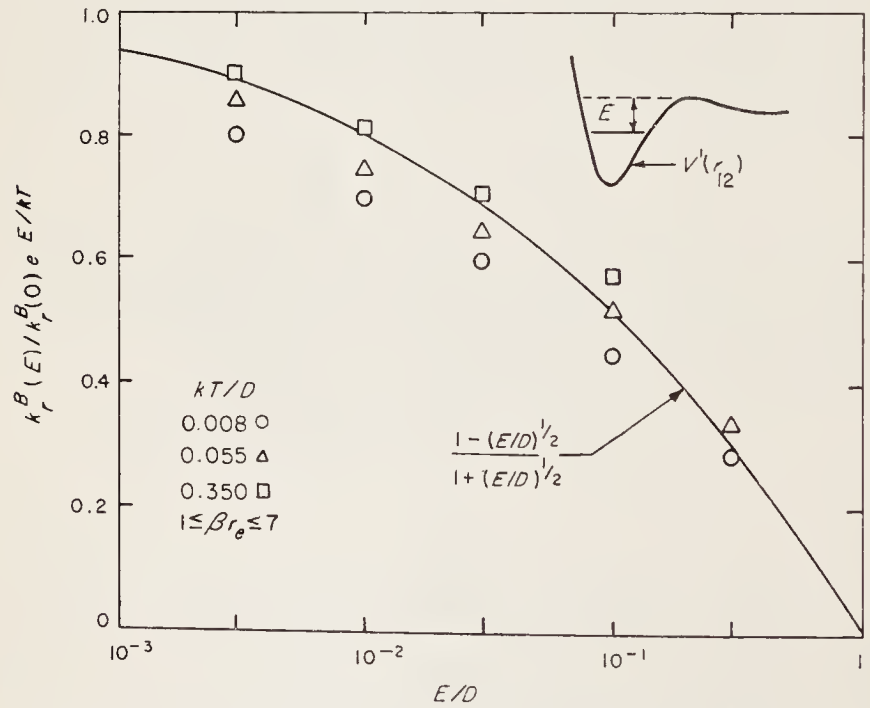

Fig. 4. Variation of the factor $k_r^B(E)$ defined by eqn. (4.59) with E/D for several values of kT/D. Note the dependence on kT/D is quite weak. The curve is the classical analogue of the square of the transition matrix elements for a Morse oscillator.

third bodies have been calculated by Woznick[23] and the writer[4] and are summarized in Fig. 4 and 5. These functions may also be used for heteronuclear molecules whose force fields are only slightly asymmetric.

For most molecules $k_r^B(E_0)$ has a weak minimum a fraction of kT below the dissociation limit, and it is an excellent approximation to evaluate $k_r^B(E_0)$ at $E_0 = 0$. A comparison of $k_r^B(0)$ with

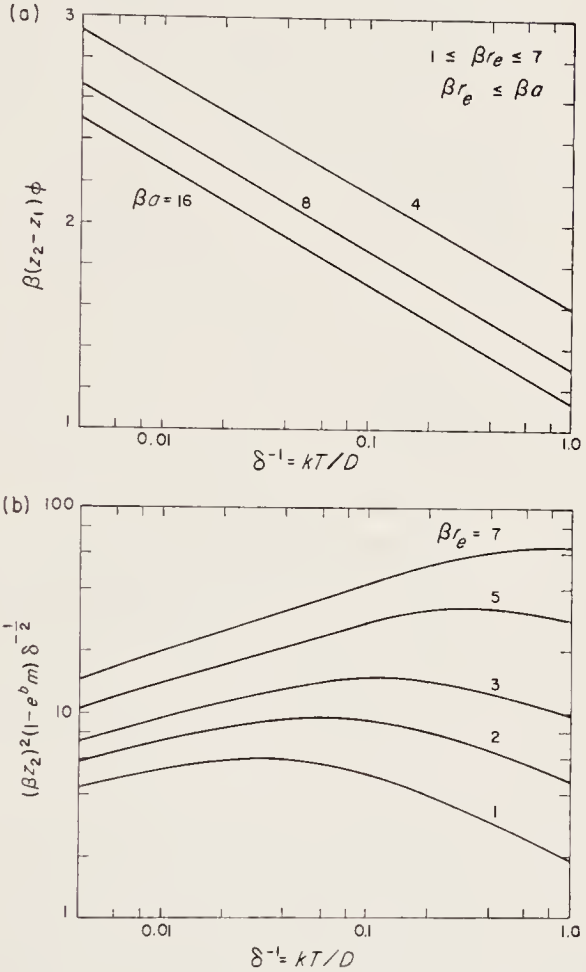

Fig. 5. Parametric curves for computing the barrier rate constant $k_r^B(0)$ for the surface tangent to the top of the rotational barrier.

the rate constants calculated previously is shown in Fig. 3. For $\mu_{12} \sim \mu_3$ it is less than either the Wigner or available energy rate constants and of the same magnitude as the three-body collision

rate constant. It is much less arbitrary than the three-body collision rate constant, however, since the effective collision volume is explicitly related to the interaction potential. This permits one to compare attractive and repulsive potentials and to investigate the relative contributions due to rotational and vibrational transitions. For example, one can see immediately from (4.54) that potentials having an attractive minimum will give a strong negative temperature coefficient for $kT \lesssim V_{3m}$.

The barrier rate constants agree quite well with flash-photolysis experiments on recombination in various gases near room temperature but overestimate the dissociation rates observed in shock tubes at high temperatures by a factor of from 3 to 10. This is, of course, not too suprising since the barrier rate is only rigorously an upper limit. What is somewhat surprising (and disappointing) is that more detailed investigations have shown that this effect can not be attributed either to recrossing corrections[24] or non-equilibrium[25] near the dissociation limit. The writer has therefore been led to the conclusion that it may be due to a failure of the "dumbbell model" which undoubtedly overestimates the angular asymmetry in the interaction potential and, therefore, overestimates the contribution from rotational transitions. Since rotational transitions dominate at high temperatures,[4] this could explain the effect. Failure of the "dumbbell model" would, of course, occur if $V_3 \neq V_{13}(r_{13}) + V_{23}(r_{23})$. This is quite likely, and calculations of the barrier rate constant with more realistic potentials should be made. In particular, the case of strongly attracting third bodies is badly in need of investigation.

V. CORRECTIONS AND EXTENSIONS

In addition to providing a systematic method for estimating rate constants, the variational theory is also a convenient starting point for the detailed numerical investigation of collision processes by Monte Carlo methods. The technique involves the random sampling of trajectories crossing the trial surface, followed by numerical integration of the equations of motion both forward and backward in time to determine the complete history of a collision. By sampling with a weight proportional to the local flow rate $\rho(\mathbf{v} \cdot \mathbf{n})$ across the surface, one obtains a statistical

distribution of trajectories which reflects their *a priori* contribution to the reaction rate. Further, by chosing surfaces which pass through the reaction zone and integrating out, one can terminate the integrations as soon as the interactions become negligible. Both these factors contribute to the overall efficiency of the calculations,

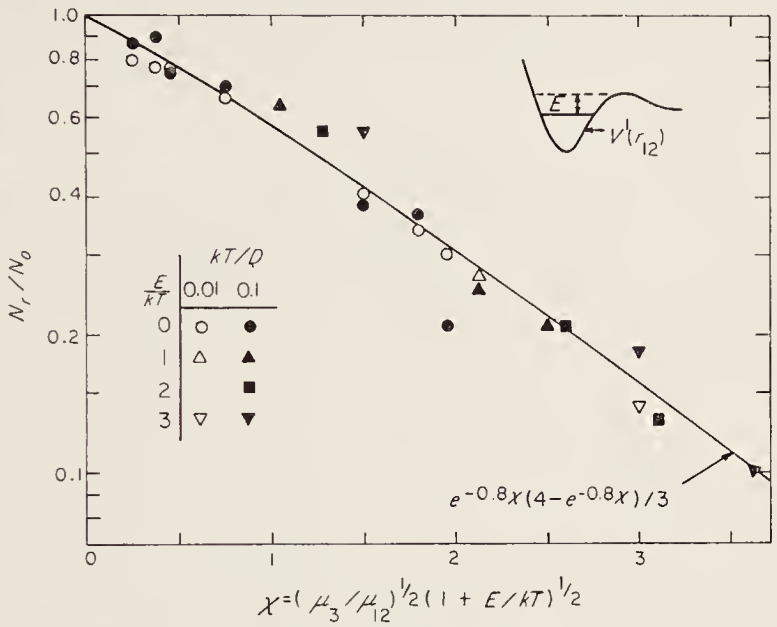

Fig. 6. Fraction of trajectories corresponding to a reaction as a function of a parameter χ for temperature $kT/D = 0{\cdot}01$ and $0{\cdot}1$ and surface $E/kT = 0$, 1, 2, and 3. The points represent calculations made for $I_2 + He$, $I_2 + Ar$, $O_2 + Ar$, $O_2 + Xe$, and $H_2 + Ar$ in the order of increasing μ_3/μ_{12}. The statistical accuracy of the data varies from 5 per cent to 10 per cent. Individual points may be identified by calculating χ from μ_3/μ_{12} and E/kT. The correlation parameter χ was arrived at empirically but is very nearly the adiabaticity parameter $\omega\tau$ for the collisions. The curve has the form expected for a linear harmonic oscillator subjected to an impulse of duration τ.

which is typically very much greater than that obtained when one samples on surfaces outside the reaction zone.

Monte Carlo methods were used by the writer[24] to investigate the recrossing correction for the trial surface at the top of the rotational barrier and extended by Woznick[26] to surfaces below the barrier. Calculations have been made for the systems $H_2 + Ar$, $O_2 + Xe$, $O_2 + Ar$, $I_2 + Ar$, and $I_2 + He$ at

temperatures, $kT/D = 0{\cdot}01$ and $0{\cdot}1$, and for surfaces $E_0/kT = 0$, 1, 2, and 3. The recrossing corrections are summarized in Fig. 6 which shows the fraction of reacting trajectories as a function of a parameter χ which is closely related to the product of the angular frequency ω of the oscillator and the collision time τ. It can be seen that this parameter correlates the results quite well and that the corrections are essentially temperature-independent. This was the basis of our statement in the preceding section that recrossing could not account for the negative temperature coefficient observed in most recombination reactions.

One of the most important facts to emerge from the calculations was that the average energy transfer in molecules undergoing dissociation or recombination is less than $\frac{1}{2}kT$. This was a sure prise to the writer who had previously thought that large energy transfer would be favored owing to the high velocity acquired by the attracting atoms as they approach one another. The reason why this is not the case is that most of the collisions with the third body occur at a time when the atoms are only weakly interacting because of the larger volume of configuration space available for distant collisions. An important corollary is that detailed conclusions about atomic collisions based on square well or truncated harmonic oscillator potentials can be grossly incorrect since these potentials have no tails where weak interactions can occur. This point is made to emphasize the need for using realistic potentials in calculations of atomic collision processes.

There is, of course, a wealth of other information about atomic collision in the results, but a discussion of this is outside the scope of this paper. The general conclusion which the writer would like to draw is, however, that the variational theory supplemented by Monte Carlo trajectory calculations is a powerful tool for investigating atomic collision processes. It is also felt that the most important weakness in the present calculations is due to the approximate potentials used, and it is hoped that further investigations in this area will lead to significant improvements.

VI. ACKNOWLEDGMENTS

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PROPERTIES OF A PARTICLE IN A ONE-DIMENSIONAL RANDOM POTENTIAL

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1. INTRODUCTION

When faced with problems which seem difficult or impossible to solve in three-dimensions, physicists have often attempted to study exactly soluble, one-dimensional models that show the most

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important features of the three-dimensional problem.† The purpose of this study of one-dimensional models is three-fold. In the first place, one obtains a qualitative picture of the solution to the problem which one hopes will carry over to the three-dimensional case. Secondly, the quantitative form of the solutions in the one-dimensional case may suggest approximate methods, which can also be applied to the original three-dimensional problem. Thirdly, if one has conceived an approximation to the three-dimensional problem, it is generally possible to test the approximation by applying it to the one-dimensional model and comparing the approximate and the exact results.

In the present article, we shall discuss some exactly solvable one-dimensional analogues of problems concerning the properties of a particle in a random potential.‡

Physicists have been interested in the electron states in such random systems as liquids and glasses, crystals with varying amounts of random impurities, and pure crystals with random deviations from periodicity due to the thermal vibrations of the lattice. Within the framework of the non-interacting electron picture, all these systems of atoms can be represented by some kind of random potential, wherein the electrons move according to the usual one-particle Schrödinger equation.

We shall not be concerned here with the problems of computing from first principles the appropriate self-consistent one-electron potentials for various positions of the atomic nuclei, or with problems of computing from first principles the statistical correlations between the nuclei. We shall be concerned only with

† Exactly soluble one-dimensional models have been studied extensively for problems involving the classical or quantum statistics of interacting particles and for problems involving the statistical mechanics of interacting spins, as well as for the properties of particles in a random potential, described in the present paper. A discussion of a model in one-dimensional statistical mechanics has already appeared in *Advances in Chemical Physics* (Prager[38]). A discussion of research in many aspects of one-dimensional physics may be found in a book by Lieb and Mattis.[28]

‡ Although all the work described in this paper has been done with the ultimate purpose of understanding three-dimensional systems, the possibility remains open that some direct applications of these techniques may be found in the study of linear polymers.

the problems of finding the properties of the electron wave functions in a given, statistically defined, random potential.

The random potential in question need not represent the full one-electron potential of the system. In an impurity problem, one may make an effective mass approximation for the electron in the perfect host crystal; each impurity is then represented by a model potential which characterizes the difference between the impurity and the host atom. Similarly, one may represent the effects of thermal fluctuations in atomic positions by a random deformation potential proportional to the local strain. The effective mass approximation can be applied, of course, to a hole, as well as to an electron. It can also be used to treat a tightly bound exciton, if one can disregard scattering of the exciton from one exciton band to another or scattering into unbound electron-hole states.

It is sometimes desirable to use neither the full Shrödinger equation nor the effective mass approximation, but rather a "one-band" approximation for the electron. In this case the position of the electron is a discrete rather than a continuous variable, and the wave function gives the probability amplitude for the electron at each lattice site. The Hamiltonian consists of terms diagonal in the electron position, and of "transfer" terms, which connect near-by sites. The coefficients of the Hamiltonian acquire random character if one supposes several kinds of atoms randomly distributed at the lattice sites, or if one considers the effects of thermal fluctuations in the distance between neighboring atoms. Once again, the particle can be a tightly bound exciton or an electron.

In the simplest discrete models, where the off-diagonal elements connect nearest-neighbor sites only, the Hamiltonian is a second-order finite-difference operator. Very similar finite-difference operators are also found when calculating the normal modes of vibration of a set of atoms with harmonic nearest-neighbor interactions. For vibrational models, randomness may occur in the spring constants, in the masses of the atoms, or in both.

We shall discuss primarily the case of a particle obeying a Schrödinger equation. The properties of a second-order finite-difference operator are in many ways similar to the properties of the Schrödinger Hamiltonian (which is a second-order differential

operator), and most of the techniques we shall discuss in the present paper have been, or can be, applied equally to a discrete model and to a continuous one-dimensional system. However, because the inclusion of a parallel set of equations for the finite-difference case would significantly lengthen this paper, we shall indicate only some of the most important results of papers dealing with finite-difference problems and shall refer the reader to the literature for details.

The simplest and most important property of the eigenstates of a particle in a random potential is the density of states as a function of the energy E, i.e., the number of eigenstates per unit energy and per unit volume of the system. The density of states directly determines the specific heat of a collection of non-interacting electrons, just as the frequency distribution of vibrational normal modes determines the specific heat of a lattice. The density of states is an important factor in many other properties of materials, among them optical absorption, photoemission, luminescence, and tunneling.

More detailed knowledge is contained in the spectral density $A(k,E)$, a function of the momentum k as well as of the energy E. The spectral density is proportional to the imaginary part of the Green's function for a particle in the random potential, and it is equal to the density of states $\rho(E)$, multiplied by the expectation value of the square of the absolute value of the k'th Fourier amplitude of the eigenfunctions at energy E. The function $A(k,E)$ is of interest because it gives us information about the wave functions themselves, as well their distribution in energy. In some models of an exciton in a disordered system, the spectral density has direct physical significance, because the line shape for optical absorption for the exciton is determined by the function $A(k,E)$ with $k = 0$.

A slightly modified spectral density for the vibrational model of a lattice determines the one-phonon contribution to inelastic scattering of neutrons by the lattice.

For many physical properties it is necessary to know "two-particle" functions for the system, which require consideration of the statistical properties of pairs of wave functions. Thus, for example, the frequency-dependent electrical conductivity of a system of non-interacting electrons in a random potential can

be expressed in terms of the function $F(E,E')$, which is equal to the product of the density of states at energy E, the density of states at energy E', and the expectation value of the square of the matrix element of the momentum operator between an eigenstate of energy E and an eigenstate of energy E'.

For most physical applications one is interested in macroscopic systems; thus one is interested in the density of states or the Green's function in the limit of an infinitely large system.

The density of states, the spectral density $A(k,E)$, and the various two-particle functions can all be calculated exactly, in one dimension, under certain conditions. Two kinds of procedures have been discovered for calculating these functions. The first kind, which we term the "analytic method," expresses the properties of the random system in terms of the solution to a set of one, two, or three integral equations. Although it has usually been necessary to solve these equations numerically, it has been possible to study them analytically in certain limiting cases. The second approach is a Monte Carlo method in which one actually studies a typical example of a long, but finite, random system. The Monte Carlo approach has been used only for calculations of the density of states. Of course, it is impossible to learn the analytic form of the density of states from a Monte Carlo calculation. Nonetheless, the procedure is "exact" because it is possible to calculate the cumulative density of states as accurately as desired by considering a sufficiently long chain.

The theory behind the procedures for calculating the density of states and Green's functions will be discussed in Sections 4–8 of this paper. References to numerical calculations which have been performed by these methods will be given in Section 9.

Various qualitative properties of one-dimensional random potentials have been carefully studied, as well as the quantitative properties mentioned above. We shall discuss in Sections 10, 11, and 12 the existence of energy gaps, the localization of energy eigenfunctions, and the vanishing of d.c. conductivity in one-dimensional random potentials.

Before beginning our discussion of the theory of the quantitative methods, we shall state the general conditions under which the analytic procedure may be used. The one-dimensional problems will then be precisely defined in Section 2, and several

examples of one-dimensional random potentials will be discussed in Section 3.

The analytic procedure for calculating the density of states, the spectral density, and the various two-particle functions, can be applied to one-dimensional potentials which obey the following two conditions:

Condition A: We require that the random potential can be broken up into a sequence of cells such that the potential in each cell is statistically independent of the potential in every other cell on the line.

Condition B: We require that the random potential in each cell involves at least one *continuous* random parameter and is a "well-behaved" function of that parameter.

Condition B is not necessary for computing the *cumulative*, or *integrated*, density of states. However, if condition B is violated, i.e., if the potential in each cell depends only on a discrete random parameter, the differential density of states and the Green's functions may not exist at all, or if they exist, may be highly discontinuous. We discuss these complications further in Section 8.

The Monte Carlo procedure for calculating the cumulative density of states does not require that the unit cells be statistically independent and is therefore more general than the analytic procedure. All that is necessary is that the statistics of the random potential be sufficiently simple, so that a long representative chain can be simulated on a computer, by means of a random-number-generating sub-routine.

2. DEFINITION OF THE MODELS

We assume that the particle obeys a Schrödinger Hamiltonian

$$H = \frac{-\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x), \tag{2.1}$$

on the line segment $0 \leqslant x \leqslant L$. We impose boundary conditions of the form

$$\psi'(0) = Z_0\psi(0), \tag{2.2}$$

$$\psi'(L) = Z_L\psi(L), \tag{2.3}$$

where Z_0 and Z_L are real constants. The line is assumed to be

divided into N unit cells such that the random potential in each cell is statistically independent of the potential in all other cells (condition A). Let x_i be the point at the right-hand end of the i'th unit cell. The i'th cell thus extends from x_{i-1} to x_i, where $x_0 = 0$, and $x_N = L$. The potential in the i'th cell is supposed to depend on one or more random parameters, which we shall represent by the single symbol λ_i. Thus we have:

$$V(x) = v(x - x_{i-1},\lambda_i), \text{ for } x_{i-1} < x < x_i, \tag{2.4}$$

and we assume that the function v does not depend on i. In general, the size of the i'th unit cell may itself be a function of λ_i:

$$x_i - x_{i-1} = l(\lambda_i). \tag{2.5}$$

We shall assume that the probability distribution for the random parameter is given by the function $p(\lambda_i)$, where p does not depend on i. The statistical model is thus characterized by the number N of unit cells, and by the functions v, l, and p.

If the length of the unit cell is not constant, then the length of the system L will itself be a random variable,

$$L = \sum_{i=1}^{N} l(\lambda_i). \tag{2.6}$$

Let us use a pair of angular brackets to denote the expectation value of a random variable for the ensemble of possible systems. Taking the expectation value of eqn. 2.6 we find

$$\begin{aligned} \langle L \rangle &= N\langle l(\lambda_i) \rangle \\ &\equiv N\bar{l}, \end{aligned} \tag{2.7}$$

where

$$\bar{l} = \int p(\lambda) l(\lambda) d\lambda. \tag{2.8}$$

If N is large, the fluctuations of L about its average value will be of order $N^{\frac{1}{2}}$, and will be negligible compared with $\langle L \rangle$.

The density of states $\rho(E)$ is defined by

$$\rho(E) \equiv \frac{1}{\langle L \rangle} \langle \sum_j \delta(E - E_j) \rangle, \tag{2.9}$$

where E_j is the energy of the j'th eigenstate of the system. We also define the cumulative density of states $N(E)$ by

$$N(E) \equiv \int_{-\infty}^{E} \rho(E') dE'. \tag{2.10}$$

The spectral density $A(k,E)$ is defined by

$$A(k,E) = \frac{1}{\langle L \rangle} \langle \sum_j |\psi_j(k)|^2 \delta(E - E_j) \rangle, \tag{2.11}$$

where $\psi_j(k)$ is the k'th Fourier coefficient of the j'th energy eigenfunction:

$$\psi_j(k) \equiv \int_0^L e^{ikx} \psi_j(x) dx. \tag{2.12}$$

The eigenfunctions $\psi_j(x)$, of course, obey the Schrödinger equation

$$(H - E_j)\psi_j(x) = 0, \tag{2.13}$$

with the normalization

$$\int_0^L \psi_j(x)^2 dx = 1. \tag{2.14}$$

[It is always possible to choose the overall phase factor for the eigenstates so that the $\psi_j(x)$ are real; we assume this has been done throughout this paper.]

The frequency-dependent electrical conductivity of a system of non-interacting spinless electrons of charge e is determined by

$$\mathrm{Re}\,\sigma(\omega) = \frac{\hbar\pi e^2}{m^2} \int_{-\infty}^{\infty} \frac{f(E) - f(E + \hbar\omega)}{\hbar\omega} F(E,E + \hbar\omega) dE, \tag{2.15}$$

where f is the Fermi function and

$$F(E,E') \equiv \frac{1}{\langle L \rangle} \left\langle \sum_{jj'} \left[\int_0^L \psi_j(x) \frac{d}{dx} \psi_{j'}(x) dx \right]^2 \delta(E - E_j)\delta(E' - E_{j'}) \right\rangle \tag{2.16}$$

(see Nakano[37]). For spin $\frac{1}{2}$ particles, an extra factor of 2 must be included in eqn. 2.15 because of the double occupancy of the states. The imaginary part of $\sigma(\omega)$ can be found from the real part by means of the well-known Kramers–Kronig relations.

The functions $\rho(E)$, $N(E)$, $A(k,E)$ and $F(E,E')$ all become independent of N, the number of unit cells, if N is sufficiently large.

3. EXAMPLES OF RANDOM SYSTEMS

Within the framework of the previous Section, many different kinds of system may be represented. We give here a number of

examples in order to illustrate the variety of systems that are possible and in order to clarify the meaning of conditions A and B of Section 1.

Example 1

A sequence of square wells of random depth. Suppose that the random potential consists of a set of square wells of a constant width a, each well separated from its successor by a length b, in which the potential $V(x)$ is equal to zero. The depth of the i'th well is a random variable λ_i. We require that the value of each λ_i be statistically independent of the values of all the others.

It is clear that the above random potential satisfies condition A. We may divide the potential into cells of length $(a + b)$, each consisting of a region of length b and potential zero, followed by a region of length a and potential $-\lambda_i$. The potential in each cell is then independent of the potential in every other cell. (Of course we could also have chosen the unit cell in various other ways: e.g., the potential well could be in the middle of the cell with a region of potential zero and length $b/2$ on each side of the well.)

The model we have just described may be used to represent a random binary alloy. In this case, each variable λ_i can take on one of two discrete values, depending on the type of atom at site i. The binary alloy, of course, will not satisfy condition B.

The model of square wells of random depth can also be used to represent, in an effective mass approximation, a deformation potential due to thermal displacements of atoms from their equilibrium positions. The variables λ_i would then have continuous distributions, usually Gaussians with variance proportional to the temperature, and the model would then satisfy condition B.

Example 2

A sequence of square wells with random distance between wells. Here we suppose that the potentials consist of a set of square wells, each of depth μ and width a, while the distance between the i'th and $(i + 1)$'th potential well is a random variable $\lambda_i \geqslant 0$. We again suppose that the variables λ_i are independent. The i'th unit cell then has length $(a + \lambda_i)$. The cell consists of a region of length a and potential $-\mu$, followed by a region of length λ_i and potential zero.

This model, with a continuous range of the variables λ_i, can be used to represent a liquid, a glass, or a solid with a thermal distribution of distances between nearest neighbors. The model may also be used to represent an impurity problem in the effective mass approximation, the pure host crystal being represented by potential zero. For impurity atoms, one should properly restrict the distances λ_i to a discrete set of values, integral multiples of a "lattice constant." For many purposes, however, it is satisfactory to treat λ_i as a continuous variable, even in the impurity model.

Example 3

A sequence of wells whose positions fluctuate about the sites on a periodic lattice. Here we again consider a sequence of square wells each of width a and depth μ. Instead of considering the *distances between wells* as independent random variables, we consider that the *positions* of the wells exhibit independent random fluctuations about their equilibria. We suppose that the equilibrium position of the center of the i'th well is at the point $x = (i - \frac{1}{2})C$, where C is the lattice constant. The actual position of the center of the well is at $x = (i - \frac{1}{2})C + \lambda_i$. Note that we require $|\lambda_i| < \frac{1}{2}(C - a)$ in order to prevent possible overlap between potentials wells. The unit cells in this model have the constant length C. The function $v(x,\lambda_i)$ consists of an interval of zero potential and length $\lambda_i + \frac{1}{2}(C - a)$, followed by an interval of length a and potential $-\mu$, followed by an interval of length $\frac{1}{2}(C - a) - \lambda_i$ and potential zero.

The model of this example has been used to represent a solid with short-range disorder due to thermal fluctuations. Note that long-range order is still preserved.

Example 4

Randomly scattered δ-functions. This is a model of an impurity system in which the impurities may occur anywhere on the line, and the positions of the impurities are statistically independent of each other. The model can be regarded as a special case of either example 1 or example 2.

Let us suppose that each δ-function has strength $-v_0$ and that the expected number of impurities per unit length is n. From the point of view of example 1, we divide the line into cells of length a,

with a very small ($na \ll 1$). The potential in each cell is $-v_0/a$ if an impurity is present, and zero otherwise. The probabilities of these situations are na and $(1 - na)$, respectively; we may neglect the possibility of two or more impurities in the same cell. The δ-function model is to be regarded as the limit of the above random potential as $a \to 0$.

Alternatively, we may formulate the model by noting that if the impurities are independently scattered on an infinite line, the distances between successive impurities are statistically independent and obey an exponential probability distribution. From the point of view of example 2, the unit cell for the model consists of a δ-function well, followed by an interval of zero potential and length λ_i, with

$$p(\lambda) = n \exp(-n\lambda). \tag{3.1}$$

Note that for finite systems, there is a slight difference between the models described in terms of example 1 or example 2. In the former example, if the number of unit cells is specified, the exact length of the system is known, but the total number of impurities is a random variable. In the second, if the number of unit cells is specified the number of impurities is known, but the total length of the system is not known exactly. In the limit of a very large system, however, the fractional fluctuations of the total number of impurities about the expected number of impurities in the first instance, or the percentage deviations of the length L from the mean $\langle L \rangle$, in the second instance, will be negligibly small. For an infinite system the two pictures are physically equivalent.

Example 5

White-Gaussian-noise-potential. This is a model in which the potential $V(x)$ obeys Gaussian statistics, with an autocorrelation function

$$\langle \Delta V(x) \Delta V(x') \rangle = \frac{D}{2} \delta(x - x'), \tag{3.2}$$

where $\Delta V(x)$ is the deviation of $V(x)$ from its average value, and D is a constant. It is called the white-noise model because the Fourier amplitudes of the potential have independent Gaussian distributions with standard deviations independent of wave-number. The white-Gaussian-noise-potential arises as a model of

a thermal deformation potential on a continuous elastic string, or as a model of a set of point impurities in the high-density limit.

As a thermal deformation potential, the white-noise model is a limiting form of example 1. Consider a model in which the unit cell is an interval of length a and depth λ_i, where λ_i obeys a continuous distribution with mean $\bar{\lambda}$ and variance

$$\langle(\lambda_i - \bar{\lambda})^2\rangle = \tfrac{1}{2}D/a. \tag{3.3}$$

The white-Gaussian-noise limit occurs if the cell size a goes to zero, while the distribution of λ_i scales according to eqn. 3.3.

As a high-density impurity band, the white-Gaussian-noise-potential is a limiting case of example 4. It is the limit of a system of independently scattered δ-functions when the concentration of impurities approaches infinity and the strength of each impurity approaches zero, such that the product nv_0^2 remains constant,

$$nv_0^2 = \tfrac{1}{2}D. \tag{3.4}$$

The Gaussian-white-noise model is of particular interest and simplicity because it contains no free parameters. For example, if the constant D is varied, all energies simply scale proportional to $D^{\frac{2}{3}}$. The density of states can be expressed simply in terms of Airy functions (Halperin[17], Lax[26]), and the numerical calculations for the spectral density $A(k,E)$ turn out to be particularly simple in this case (Halperin[17]). Simple asymptotic forms for $A(k,E)$ can be found in the limits where $E \to \pm\infty$.

The examples we have just given are merely the simplest cases of potentials obeying condition A. The reader may readily think of many more. It is clear, for instance, that there is no necessity for using square wells in examples 1–3, any shape potential of finite spatial extent would be permissible. Also, the binary alloy represented by example 1 can be generalized to consider unit cells with variable width as well as depth. Finally, of course, it is possible to combine various types of disorder in one unit cell. The unit cell would then depend on several random parameters, instead of the single parameter λ_i.

4. ANALYTIC METHOD—GENERAL CONSIDERATIONS

The analytic methods for calculating the density of states or the Green's functions can all be characterized as follows. One

defines a set of variables $\{\mathbf{Q}_i\}$ which depend on the cell index i and also on the energy E and on any other parameters of the problem (such as k in the case of the spectral density). The $\mathbf{Q}_i$ are also defined to depend on the random potential $V(x)$ and are therefore themselves random variables. The symbol $\mathbf{Q}_i$ may represent a simple real variable, or a set of several real variables, depending on the problem.

Let $P_i(\mathbf{Q}_i)$ be the probability distribution of $\mathbf{Q}_i$. The quantity we are seeking, the density of states or the Green's function, will be expressed either in terms of the function P_N or in terms of the average over i of the functions P_i. Our principal task will be to compute these functions. In the limit of an infinite system, it will suffice to know the limiting form of these functions as i becomes large. (Also, for Green's-function problems, we shall obtain important mathematical simplifications because it suffices to consider certain moments of these distributions.)

The variables $\mathbf{Q}_i$ are defined in such a manner, that $\mathbf{Q}_i$ is completely determined if one knows the potential in the i'th unit cell, and the value of $\mathbf{Q}_{i-1}$. Thus we may write

$$\mathbf{Q}_i = \mathbf{R}(\mathbf{Q}_{i-1},\lambda_i), \tag{4.1}$$

where $\mathbf{R}$ is a known function.

If the random potential satisfies condition A of section 1, i.e., if λ_i is statistically independent of λ_j for $j \neq i$, then the variables $\mathbf{Q}_i$ are said to form a "Markoff process". The probability densities $P_i(\mathbf{Q}_i)$ can then be calculated by an iterative procedure:

$$P_i(\mathbf{Q}_i) = \int K(\mathbf{Q}_i,\mathbf{Q}_{i-1}) P_{i-1}(\mathbf{Q}_{i-1}) d\mathbf{Q}_{i-1}, \tag{4.2}$$

where the kernel K is given by

$$K(\mathbf{Q}_i,\mathbf{Q}_{i-1}) \equiv \int \delta[\mathbf{Q}_i - \mathbf{R}(\mathbf{Q}_{i-1},\lambda_i)] p(\lambda_i) d\lambda_i. \tag{4.3}$$

[The variables $\mathbf{Q}_i$ are defined in such a way that the initial distribution $P_1(\mathbf{Q}_1)$ is known.]

5. THE CUMULATIVE DENSITY OF STATES

A. Node Counting

The simplest property to calculate, and the one which has been studied most intensively, is the cumulative density of states

$N(E)$. The method of calculation uses a well-known theorem (see, for example, Schmidt[40]). Let $\phi(x)$ be the solution of the Schrödinger differential equation at energy E,

$$\frac{-\hbar^2}{2m}\phi''(x) + V(x)\phi(x) = E\phi(x), \tag{5.1}$$

with the "initial conditions"

$$\phi(0) = 1, \tag{5.2}$$

$$\phi'(0) = Z_0. \tag{5.3}$$

Then the number of *eigenvalues* of the Schrödinger equation with energy less than E is equal to the number of *zeros* of the function $\phi(x)$ in the interval $0 < x < L$ (except for a possible error of ± 1, depending on the boundary condition at L). Thus, except for a possible error of order $(1/L)$, the cumulative density of states is equal to the expectation value of the number of zeros per unit length in $\phi(x)$. (For vibrational normal modes or other problems in which the wave function is defined only at discrete set of points, one must count the number of sign changes in the wave function ϕ.)

Note that the functions ϕ will *not*, in general, be eigenfunctions of the Hamiltonian, because they will not satisfy the final condition (2.3), that the logarithmic derivative of $\phi(x)$ should equal Z_L at $x = L$, unless the energy E happens to be an eigenvalue of the Hamiltonian.

B. Monte Carlo Method

The Monte Carlo method of calculating the cumulative density of states is in principle very simple. One generates on a computer a representative random chain of N cells, where N is a large finite number. One then computes the function $\phi(x)$ in this chain, for a number of different energies E, and one counts the number of zeros. It is not difficult to prove that the number of zeros per unit length is an ergodic quantity, i.e., that the number of zeros per unit length of a particular, sufficiently long chain will be approximately equal to the expected number of zeros per unit length. The error in $N(E)$ resulting from a Monte Carlo calculation will be of order $N^{-\frac{1}{2}}$ as $N \to \infty$. With modern high-speed computers, it is qutie feasible to study chains of 10^5 or more unit cells,

and the Monte Carlo method will generally be adequate, except in energy ranges where the density of states itself is very small. Note that the method of counting zeros in $\phi(x)$ for a small number of energies E is very much simpler, for a long chain, than trying to locate all the eigenvalues of the Hamiltonian.

The Monte Carlo method was first applied to a random potential problem by James and Ginzbarg[22], in 1953.

In applying the Monte Carlo method, one need not resort to numerical integration of the differential eqn. 5.1. In any simple model, we know the general solution of the differential equation in any one unit cell, for any given value of the parameter λ_i. The problem of computing $\phi(x)$ is then simply one of matching ϕ and ϕ' at the boundaries between unit cells. In particular, since expression 5.1 is a homogeneous linear equation, ϕ and ϕ' at x_i will be linearly related to ϕ and ϕ' at x_{i-1}. We write

$$\begin{pmatrix} \phi' \\ \phi \end{pmatrix}_{|x=x_i} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} \phi' \\ \phi \end{pmatrix}_{|x=x_{i-1}}, \tag{5.4}$$

where the matrix $\mathbf{M}$ depends on the parameter λ_i and the energy E. We call $\mathbf{M}$ the *transfer matrix* for the i'th cell. It is convenient to define the variables $z_i \equiv z(x_i)$, where

$$z(x) \equiv \phi'(x)/\phi(x). \tag{5.5}$$

In the i'th unit cell, the function $\phi(x)$ is determined, except for an overall multiplicative constant, by the values of λ_i and z_{i-1}. Thus it is clear that n_i, the number of zeros in the i'th unit cell, is a function only of λ_i and z_{i-1}:

$$n_i = n(z_{i-1},\lambda_i) \tag{5.6}$$

Similarly we may write

$$z_i = R(z_{i-1},\lambda_i). \tag{5.7}$$

From expression 5.4 we can write an explicit form for R:

$$R(z,\lambda_i) = (M_{11}z + M_{12})/(M_{21}z + M_{22}). \tag{5.8}$$

It is also possible to write an explicit expression for n. It can be shown that $n(z,\lambda_i)$ is a step function,

$$\begin{aligned} n(z,\lambda_i) &= \nu(\lambda_i), \text{ for } z \geqslant \zeta(\lambda_i), \\ &= \nu(\lambda_i) + 1, \text{ for } z < \zeta(\lambda_i), \end{aligned} \tag{5.9}$$

where $\nu(\lambda_i)$ is the number of zeros in the wave function with $z_{i-1} = +\infty$, and

$$\zeta(\lambda_i) = -M_{22}/M_{21}. \tag{5.10}$$

The Monte Carlo procedure for counting the nodes in ϕ can now be reduced to a very simple iterative procedure. Assume that we know the value of z_{i-1}. Using a random number generator we pick λ_i. We then calculate n_i and z_i from eqn. 5.6 and 5.7, and repeat the process for the next cell. For greatest efficiency, of course, we carry out the iteration simultaneously for all the values of E at which we wish to compute the density of states.

For a random system governed by a second-order finite difference operator, the procedure for calculating $N(E)$ is essentially identical with the above. The major change is that we must use the finite difference $\phi(i) - \phi(i-1)$ instead of the derivative $\phi'(x_i)$ in (5.4) and (5.5). Also, in some finite-difference models, the matrix $\mathbf{M}$ will depend on λ_{i-1} as well as λ_i.

C. Analytic Method

We now turn to the analytic method of calculating $N(E)$ which was first described by Schmidt[40], in 1957. If the parameter λ_i is statistically independent of the random parameters of all the other cells, we can immediately use the general technique of Section 4. We need only identify the Markoff variable $\mathbf{Q}_i$ with z_i. The expected number of zeros in the i'th unit cell is clearly given by

$$\langle n_i \rangle = \int_{-\infty}^{\infty} n(z) P_{i-1}(z) dz, \tag{5.11}$$

where

$$n(z) \equiv \int p(\lambda_i) n(z, \lambda_i) d\lambda_i \omega. \tag{5.12}$$

The probability distributions P_i are determined by induction, according to eqn. 4.2. In general, if the random potential satisfies condition B of section 1, the probability distributions $P_i(z)$ will converge to a limiting distribution $P(z)$ independent of i and of the initial value Z_0, as i becomes large. In this case, the value of $\langle n_i \rangle$ becomes independent of i, if i is sufficiently large; we find that for an infinite system:

$$N(E) = \bar{l}^{-1} \int_{-\infty}^{\infty} n(z) P(z) dz. \tag{5.13}$$

If we substitute the limiting function P for P_i and P_{i-1} in eqn. 4.2, we obtain the integral equation

$$P(z) = \int_{-\infty}^{\infty} K(z,z')P(z')dz', \tag{5.14}$$

where K is the kernel defined by eqn. 4.3, after identification of the function $\mathbf{R}$ with R of equation 5.8:

$$K(z,z') = \int \delta[z - R(z',\lambda)]p(\lambda)d\lambda. \tag{5.15}$$

The function $P(z)$ is uniquely determined by expression 5.14 together with the normalization condition

$$\int_{-\infty}^{\infty} P(z)dz = 1. \tag{5.16}$$

The analytic method for calculating $N(E)$ can be summarized as follows. For each value of E we must compute the functions $n(z)$ and $K(z,z')$ according to eqn. 5.12 and 5.15. We then must solve the integral equation 5.14 and use 5.13 to find $N(E)$. Note that the integral equation 5.14 can always be solved on a computer by iteration, since we know that $P_i(z)$ converges to $P(z)$.

When we consider models, such as the white-Gaussian-noise model, in which the unit cell is infinitesimal, certain changes must be made in the equations of this section (Frisch and Lloyd[15]). For example, equation 5.13 will be replaced by

$$N(E) = \lim_{z\to\infty} z^2 P(z). \tag{5.17}$$

Equation 5.14 will also be changed in form. For the white-Gaussian-noise model, it becomes a second-order linear differential equation.

6. GREEN'S FUNCTIONS

A. Momentum-dependent Spectral Density

The analytic procedure for calculating the cumulative density of states $N(E)$ used the trick of counting zeros in order to express the answer in terms of the probability distribution of a Markoff variable. In order to do the same for $A(k,E)$, we must use a more elaborate procedure.

Equation 2.11, which defines $A(k,E)$, can be written

$$A(k,E) = \frac{1}{\langle L \rangle} \left\langle \frac{\left| \int_0^L \phi(x) e^{ikx} dx \right|^2}{\int_0^L \phi(x)^2 dx} \sum_j \delta(E - E_j) \right\rangle. \tag{6.1}$$

The energies E_j are the eigenvalues of the Hamiltonian. The δ-function in eqn. 6.1 will therefore be satisfied if, and only if, the logarithmic derivative of $\phi(x)$ is equal to Z_L when $x = L$. Thus we may change the variable in the δ-function from E to $z(L)$ by writing

$$\sum_j \delta(E - E_j) = \delta[Z_L - z(L)] \left| \frac{\partial z(L)}{\partial E} \right|. \tag{6.2}$$

It is convenient to define three functions

$$U_1(x) \equiv \int_0^x e^{ikx'} \phi(x') dx' / e^{ikx} \phi(x), \tag{6.3}$$

$$U_2(x) \equiv \int_0^x \phi(x')^2 dx' / \phi(x)^2, \tag{6.4}$$

$$U_3(x) \equiv \partial z(x) / \partial E. \tag{6.5}$$

Equation 6.1 can now be written

$$A(k,E) = \frac{1}{\langle L \rangle} \left\langle \frac{|U_1(L)|^2}{U_2(L)} |U_3(L)| \delta[Z_L - z(L)] \right\rangle. \tag{6.6}$$

Thus $A(k,E)$ is expressible in terms of the joint probability distribution of the four variables $z(x)$ and $U_\alpha(x)$, $(\alpha = 1, 2, 3)$, at the point $x = L = x_N$.

We shall be interested in the functions z and U_α at the points $x = x_i$, where x_i is the end-point of the i'th unit cell. It may be readily verified that the U_α obey iterative equations of the form

$$U_\alpha(x_i) = S_\alpha(z_{i-1}, \lambda_i) + T_\alpha(z_{i-1}, \lambda_i) U_\alpha(x_{i-1}), \tag{6.7}$$

where the quantities S_α and T_α depend only on the random potential in the i'th unit cell, and the value of $z(x_{i-1})$. For example, for $\alpha = 1$ we have

$$S_1 = \int_{x_{i-1}}^{x_i} e^{ik(x - x_i)} [\phi(x)/\phi(x_i)] dx, \tag{6.8}$$

$$T_1 = e^{ik(x_{i-1} - x_i)} [\phi(x_{i-1})/\phi(x_i)]. \tag{6.9}$$

The ratio $\phi(x)/\phi(x_i)$ is, of course, determined by z_{i-1} and λ_i if x falls in the i'th unit cell.

It is clear that the set of four variables $\{z(x_i),U_\alpha(x_i)\}$ forms a Markoff process, and, in theory at least, the value of $A(k,E)$ can be found by straightforward application of the general procedure of section 4. To work with a probability distribution of four variables would, however, be exceedingly difficult and it is fortunate that some major simplifications are possible.* The first simplification occurs because, by a happy coincidence,

$$U_3(x) \equiv \frac{-2m}{\hbar^2} U_2(x) \tag{6.10}$$

regardless of the form of the potential $V(x)$ (for a proof of this identity, see Halperin[17]). Equation 6.6 can thus be simplified to

$$A(k,E) = \frac{2m}{\hbar^2\langle L\rangle}\langle|U_1(x_N)|^2\delta[z_L - z(x_N)]\rangle. \tag{6.11}$$

Thus we need only find the joint probability density of the Markoffian pair of variables $\{z(x_i),U_1(x_i)\}$.

Still further simplification is possible, however, because equation 6.7 is linear in U_1. We find that it is unnecessary to work with the complete joint distribution of z and U_1 because a closed set of iterative equations may be derived for the zeroth, first, and second moments of the distribution with respect to U_1. The moments in question are defined by

$$\Omega_0(z,i) \equiv \langle\delta[z - z(x_i)]\rangle, \tag{6.12}$$

$$\Omega_1(z,i) \equiv \langle U_1(x_i)\delta[z - z(x_i)]\rangle, \tag{6.13}$$

and

$$\Omega_2(z,i) \equiv \langle|U_1(x_i)|^2\delta[z - z(x_i)]\rangle. \tag{6.14}$$

The spectral density, of course, is expressed in terms of the second moment, at $i = N$:

$$A(k,E) = \frac{2m}{\hbar^2\langle L\rangle}\Omega_2(Z_L,N). \tag{6.15}$$

The function $\Omega_0(z,i)$ is just the probability distribution of $z(x_i)$. It is identically equal to the function $P_i(z)$ of section 5, and can,

* When the parameter k is not equal to zero, the set of four quantities is actually a set of five *real* variables, as U_1 will have both a real and an imaginary part.

therefore, be found from the iterative equation 4.2. In the following sections we shall use the notations $P_i(z)$ and $\Omega_0(z,i)$ interchangeably.

Using equation 6.7 we also find iterative equations for Ω_1 and Ω_2:

$$\Omega_1(z,i) = \int_{-\infty}^{\infty} [K_{11}(z,z')\Omega_1(z',i-1) + K_{10}(z,z')\Omega_0(z',i-1)]dz', \tag{6.16}$$

$$\Omega_2(z,i) = \int_{-\infty}^{\infty} [K_{22}(z,z')\Omega_2(z',i-1) + K_{20}\Omega_0(z',i-1) + 2\mathrm{Re}\, K_{21}(z,z')\Omega_1(z',i-1)]dz', \tag{6.17}$$

where

$$K_{11}(z,z') \equiv \int T_1(z',\lambda_i)\delta[z - R(z',\lambda_i)]p(\lambda_i)d\lambda_i, \tag{6.18}$$

$$K_{10}(z,z') \equiv \int S_1(z',\lambda_i)\delta[z - R(z',\lambda_i)]p(\lambda_i)d\lambda_i, \tag{6.19}$$

$$K_{22}(z,z') \equiv \int |T_1(z',\lambda_i)|^2\delta[z - R(z',\lambda_i)]p(\lambda_i)d\lambda_i, \tag{6.20}$$

$$K_{20}(z,z') \equiv \int |S_1(z',\lambda_i)|^2\delta[z - R(z',\lambda_i)]p(\lambda_i)d\lambda_i, \tag{6.21}$$

$$K_{21}(z,z') \equiv \int S_1(z',\lambda_i)^* T_1(z',\lambda_i)\delta[z - R(z',\lambda_i)]p(\lambda_i)d\lambda_i. \tag{6.22}$$

We have already noted in section 5, that for random potentials satisfying condition B, the probability distribution $\Omega_0(z,i)$ approaches a limit, $\Omega_0(z)$ independent of i, when $i \to \infty$. Under the same conditions we find that $\Omega_1(z,i)$ approaches a limit $\Omega_1(z)$, independent of i. The limiting function $\Omega_0(z)$ is determined by the integral equation 5.14 with the normalization (5.16). The function $\Omega_1(z)$ is determined, similarly, by the integral equation

$$\Omega_1(z) = \int [K_{11}(z,z')\Omega_1(z') + K_{10}(z,z')\Omega_0(z')]dz', \tag{6.23}$$

which occurs after substituting the limiting forms of Ω_0 and Ω_1 in both sides of eqn. 6.16.

The function Ω_2 does not become independent of i, for large i. Instead, we find that; for large i,

$$\Omega_2(z,i) \sim iC + f(z), \tag{6.24}$$

where C is a constant, independent of i and z, and f is a function independent of i. The value of the constant C is given by

$$C = \int g(z)[K_{20}(z,z')\Omega_0(z') + 2\mathrm{Re}\, K_{21}(z,z')\Omega_1(z')]dzdz', \quad (6.25)$$

where $g(z)$ is the unique solution of the integral equation

$$g(z') = \int g(z)K_{22}(z,z')dz, \quad (6.26)$$

with the normalization

$$\int g(z')dz' = 1. \quad (6.27)$$

The spectral density for a very long system is given by

$$A(k,E) = \frac{2mC}{\hbar^2 \bar{l}}. \quad (6.28)$$

As expected, the spectral density is then independent of the length of the system and is independent of the boundary condition Z_L.

The function $g(z)$ has an interesting physical interpretation. It can be shown that $g(z)$ is the limiting form of the probability distribution for $z(x_i)$ which would have occured if the value of $z(x)$ had been fixed at x_N instead of $x = 0$. As discussed in section 11, $g(z)$ is *not*, in general, equal to $\Omega_0(z)$. If the random potential in each unit cell is symmetric about the center of the cell (or if the *statistical ensemble* of unit cells is invariant under reflection), then $g(z)$ is related to $\Omega_0(z)$ by

$$g(z) = \Omega_0(-z). \quad (6.29)$$

In this case it is not necessary to solve the integral equation 6.26. With many other models, such as those in example 2 of section 3, equation 6.29 does not hold, but a somewhat more complicated expression giving g in terms of Ω_0, can be derived, which also eliminates the need for solving directly the integral equation 6.26.

Let us summarize the steps necessary to calculate the spectral density for a particular value of k and E. One must first calculate the kernels K, K_{10}, K_{11}, etc., according to eqn. 5.15 and 6.18–6.22. Then one must solve the integral equations 5.14 and 6.23 and, if necessary, 6.26, to find $\Omega_0(z)$, $\Omega_1(z)$ and $g(z)$. Finally, one uses eqn. 6.25 and 6.28 to find $A(k,E)$. The entire procedure must be

repeated for each new value of k and E, except that the functions $\Omega_0(z)$ and $g(z)$ are independent of k. In the white-Gaussian-noise model, eqn. 5.14 and 6.23 are replaced by second-order differential equations, and the evaluation of the spectral density is particularly simple.

B. Frequency-dependent Electrical Conductivity

In order to find the electrical conductivity $\sigma(\omega)$, we must find the function $F(E,E')$ defined by eqn. 2.16. This function can be found by a procedure very similar in principle to that used to find the spectral density. Because we must simultaneously consider the functions $\phi(x)$, and $z(x)$ at two different energies, E and E', we shall now make explicit the energy dependence of these functions.

We define a new function

$$W(x) = \frac{\int_0^x \phi(x',E) \frac{d}{dx'} \phi(x',E')dx'}{\phi(x,E)\phi(x,E')}. \tag{6.30}$$

It may be seen that $W(x_i)$ is related to $W(x_{i-1})$ by

$$W(x_i) = S + TW(x_{i-1}), \tag{6.31}$$

where S and T depend on the random parameter λ_i and on the values of $z(x_{i-1},E)$ and $z(x_{i-1},E')$. Thus it is clear that the three variables $z(x_i,E)$, $z(x_i,E')$, and $W(x_i)$ form a Markoff process, and the joint probability distributions of these variables could be calculated by an interative process of the form 4.2. We define the zeroth, first, and second moments, with respect to W, of the probability distributions by

$$\Omega_\mu(z,z',i) \equiv \langle W(x_i)^\mu \delta[z - z(x_i,E)]\delta[z' - z(x_i,E')]\rangle, \ \mu = 0,1,2. \tag{6.32}$$

The reader may readily verify by methods similar to those used to derive eqn. 6.11, that

$$F(E,E') = \frac{1}{\langle L \rangle} \left(\frac{2m}{\hbar^2}\right)^2 \Omega_2(Z_L,Z_L,N). \tag{6.33}$$

As in the case of the spectral density, it is nct necessary to solve the iterative equations for the complete probability distribution of $z(x_i,E)$, $z(x_i,E')$, and $W(x_i)$. Because eqn. 6.31 is linear in W, a closed set of equations may be found expressing Ω_0, Ω_1, and Ω_2 at the point i in terms of the functions at $i-1$. These equations are integral relations, similar to 6.16 and 6.17. Now, however, the kernels are functions of four variables z, z', z'', and z''', and the integrals must be performed over two variables, z'' and z'''. Again one finds that Ω_0 and Ω_1 approach limits independent of i as $i \to \infty$, provided that the random potential obeys condition B, and provided that $E \neq E'$. Under these same conditions one finds that Ω_2/i approaches a constant, independent of z, z', and i, as $i \to \infty$. The value of $F(E,E')$ is found by solving integral equations similar to eqn. 5.14, 6.23, and 6.26, and evaluating an integral similar to 6.25. Unfortunately, the amount of computation necessary to calculate two particle functions such as $F(E,E')$ is much greater than that necessary to find $A(k,E)$, because the integral equations are equations of two variables instead of one. As yet, no attempt has been made to calculate the electrical conductivity for any model.

It should be noted that the method outlined above cannot be used directly to calculate the conductivity for zero frequency. In order to find the d.c. conductivity we must study the limiting form of the function $F(E,E+\hbar\omega)$ for finite ω, as $\omega \to 0$ (see section 12).

7. ALTERNATE ANALYTIC PROCEDURES FOR THE DENSITY OF STATES

In order to calculate the density of states function $\rho(E)$, by the methods of Section 5, one is forced to use an indirect procedure. One must first calculate the cumulative density of states $N(E)$, and then numerically differentiate. It is also possible to calculate $\rho(E)$ directly by a method similar to those used to calculate $A(k,E)$ and the electrical conductivity. The reader may readily verify, by the same techniques used to derive eqn. 6.6, that

$$\rho(E) = \frac{1}{\langle L \rangle} \langle |U_3(x_N)| \delta[Z_L - z(x_N)] \rangle, \tag{7.1}$$

where U_3 is defined by eqn. 6.5. Thus the density of states is expressed in terms of the first moment with respect to U_3 of the joint probability distribution of U_3 and z at x_N. An iterative integral equation may be derived which expresses the first moment at x_i in terms of the first moment at x_{i-1} and the probability distribution $P_{i-1}(z)$. One finds finally, that for large systems,

$$\rho(E) = \frac{1}{\bar{l}} \int g(z)\kappa(z,z')P(z')dzdz', \tag{7.2}$$

where $g(z)$ and $P(z)$ are the same as in Sections 5 and 6, and the kernel κ is a function which can be readily determined by studying the solutions of the Schrödinger equation in a single unit cell.

For completeness, we should mention another procedure which can be used for calculating the density of states for an electron or for a phonon in a disordered system. This is the method proposed by Dyson[14] in 1953, which was historically the first of the analytic methods for solving these problems. Dyson's method is, however, both conceptually more difficult and numerically less tractable than either of the two methods presented above, and we shall not attempt to describe it here. The method has been successfully applied only to one, rather artificial, phonon model.

Domb *et al.*[12a] have proposed a method for calculating exactly all the moments of the vibrational frequency distribution for a disordered chain. If all the moments are known, the frequency distribution can be calculated, in principle, as accurately as desired, by using an appropriate inversion procedure. Unfortunately, in many of the regions of interest, the inversion procedures appear to converge very slowly and calculations using a small number of moments are, in practice, an "approximate" rather than an "exact" technique.

The method proposed by Faulkner and Korringa[14c] for calculating the electronic density of states in a random binary alloy, which was originally presented as an exact method, is actually incorrect, although it appears to be a good approximation in many cases. The error in Faulkner and Korringa's procedure arises from an unjustified replacement of a non-ergodic quantity by its ensemble average (see discussions by Faulkner[14b] and Lieb and Mattis[28]).

8. DIFFERENCE BETWEEN DISCRETE AND CONTINUOUS RANDOM PARAMETERS

In the previous Sections, we have assumed that the probability distributions $P_i(z)$ converge to a final distribution $P(z)$ which is independent of the initial value Z_0, provided that the random potential satisfies condition B. A rigorous and general proof that this is the case has never been given; in fact, one can devise models which obey condition B, but for which there is lack of convergence at certain special energies. Nonetheless, one can derive a number of powerful theorems which guarantee the convergence of the probability distribution provided the transfer matrix **M** meets certain general requirements, as a function of the continuous random parameter. (One such set of convergence conditions is given in the Appendix to this paper.) It seems highly probable that every reasonable unit cell which depends on one or more continuous random parameters will give rise to a transfer matrix that satisfies these conditions, except possibly at a number of isolated special energies. (Of course we must exclude models in which the random potential is, in fact, independent of the continuous random parameter in some range, or where the probability distribution of the random parameter is too singular.)

It is useful to distinguish between a "bounded" model, in which there is a finite upper bound to the length of the unit cell and to the magnitude of the random potential (or of any δ-function singularities), and an "unbounded" model, in which one or more of these quantities is unbounded. In the bounded case, we generally find that the limiting distribution $P(z)$ is continuous. The unbounded case will be as well behaved as the bounded case if the probability distribution of the random parameter falls off quickly-enough at infinity. If the probability distribution falls off exponentially or more slowly, as the length of the unit cell or the magnitude of the potential becomes infinite, then $P(z)$, as well as the various $P_i(z)$, may be infinite at certain values of z. These singularities will not cause difficulty except, possibly, at certain isolated energies.

The situation is entirely different for models which do not satisfy condition B. For example, if the random parameter has two possible values, it is clear that $P_1(z)$ will then be a sum of

two δ-functions, $P_2(z)$ will be a sum of four δ-functions, $P_3(z)$ will be a sum of eight δ-functions, etc. In a strict sense, the functions $P_i(z)$ cannot converge, and it is more useful to discuss the integrated probability distributions $S_i(z)$, defined by

$$S_i(z) = \int_{-\infty}^{z} P_i(z')dz'. \tag{8.1}$$

In general, the functions $S_i(z)$ do converge to a continuous limiting function $S(z)$, except possibly at isolated special energies. If the limiting function $S(z)$ has a continuous derivative one can define $P(z)$ to be the derivative of $S(z)$; the function thus defined will satisfy eqn. 5.14, and can be determined from 5.14 and the normalization 5.16. It is then permissible to use this function $P(z)$ in eqn. 5.13 to find the cumulative density of states, $N(E)$. We may also hope to define $\Omega_1(z)$ and $g(z)$ by a similar procedure, in which case we may use eqn. 7.2 or 6.25 to calculate $\rho(E)$ or $A(k,E)$. Unfortunately the function $S(z)$ will not always be differentiable. Schmidt[40] showed that under certain conditions the derivative $P(z)$, if it exists at all, must be extremely discontinuous, being infinite or zero at a dense set of points on the line

$$-\infty < z < \infty.$$

The cumulative density of states can be calculated even if $P(z)$ does not exist. The function $n(z)$ in eqn. 5.13 will be a sum of step functions, if the unit cell depends on a discrete random parameter. Equation 5.13 can therefore be integrated by parts to give $N(E)$ directly in terms of the values of $S(z)$ at a discrete set of points. However, eqn. 6.25 and 7.2 cannot be simplified by integrations by parts, because the kernels of these equations already involve δ-functions. Thus it may not be possible to calculate $\rho(E)$ and $A(k,E)$.

It has been discovered, in fact, that the density of states and the spectral density do not always exist. Although the cumulative density of states $N(E)$ will always be continuous, it will not necessarily be differentiable. Agacy and Borland[2] have calculated histograms of $[N(E + \Delta E) - N(E)]/\Delta E$ for a binary alloy of δ-functions and have found very irregular behavior in certain energy ranges. (See Figs. 1 and 2.) Similar calculations for a random chain of atoms of two kinds of mass have also revealed

irregular behavior in the vibrational mode distribution when the ratio of masses is sufficiently different from 1 and when the concentration of light atoms is not too great (Dean[8,9], Agacy[1]) (see Fig. 3). In the vibrational problem, a peak in the normal mode distribution occurs at roughly the frequency of vibration of an isolated light atom in a chain of heavy atoms. Similar, smaller peaks occur at the frequencies of a pair of adjacent light atoms, of a pair of light atoms separated by one heavy atom, etc. In the electronic problem, one also finds peaks that may be associated with an isolated atom of one type, with a pair of atoms, etc. There are also peaks which do not appear to have such a simple explanation. Pronounced peaks have been observed, primarily, in energy or frequency ranges that are forbidden for a pure lattice of one component but not for a pure lattice of the other component. The presence of these peaks is an indication of eigenfunctions that are localized at a cluster of one or two impurity atoms. More detailed explanations of these peaks have been presented by Hori[19] and by Hori and Fukushima[21]. There also may be frequencies at which the density of states vanishes (Matsuda[34], Hori[20]).

The fact that one finds peaks in a histogram of the distribution of states does not, of course, imply that there are mathematical singularities in the density of states. Nonetheless, one can give a rigorous argument that this will be the case, in certain ranges of concentration and energy. Let us discuss the simple example of a lattice in which the unit cell has length a and may consist either of an interval of zero potential or of a similar interval with a δ-function well in the center. Let us denote the probability of the δ-function "impurity" by p. An isolated δ-function at a point y will have a bound-state wave function of the form

$$\psi(x) = \kappa^{1/2} e^{-\kappa|x-y|}, \tag{8.2}$$

where κ is related to the energy, E_0, of the wave function by

$$E_0 = -\hbar^2\kappa^2/2m. \tag{8.3}$$

If other δ-functions are present on the line, then the energy of the wave function will be shifted by an amount ΔE which, we expect intuitively, will be proportional to the overlap of the wave function

with the nearest-neighbor potential. Rigorously, if there is no impurity within a distance s of the i'th impurity, we can construct a "wave packet" $f(x)$ that is centered at the i'th impurity, which vanishes outside the interval $\pm s$ about the impurity, and such that

$$\int f(x)(H - E_0)^2 f(x)dx < C^2 \, e^{-2\kappa s}, \tag{8.4}$$

where C is a constant independent of s.

If we can find M δ-functions in the crystal such that no two are neighboring impurities, and such that, for each, the nearest-neighbor impurity is at least a distance s away, then we can construct M orthogonal wave packets such that expression 8.4 holds for each of them. By expanding 8.4 in terms of the eigenfunctions of H, it is not difficult to prove that there must be at least $\frac{1}{2}M$ eigenfunctions such that

$$|E_j - E_0| < 2C \, e^{-\kappa s}. \tag{8.5}$$

In a long crystal the number of impurities, per unit length, with nearest-neighbors further away than s will be approximately equal to $(1 - p)^{2s/a} p a^{-1}$. Thus if ΔE is in the range $0 \leqslant \Delta E \leqslant 2C$, we must have

$$N(E_0 + \Delta E) - N(E_0 - \Delta E) > \left[\frac{p}{2^{\gamma+2} C^\gamma a}\right] (\Delta E)^\gamma, \tag{8.6}$$

where

$$\gamma \equiv \frac{2}{\kappa a} |\log (1 - p)| \approx \frac{2p}{\kappa a} + \frac{p^2}{\kappa a} + \ldots \tag{8.7}$$

Dividing both sides of (8.6) by ΔE and taking the limit as $\Delta E \to 0$, we see that $\rho(E_0)$ must be infinite if $\gamma < 1$. This will be the case whenever the concentration of impurities is sufficiently small.

By reasoning similar to the above, we find singularities at the energies of the bound states of two consecutive δ-functions, of two δ-functions with one space between them, of three consecutive δ-functions, etc. In short, we shall find an infinite density of singularities throughout a finite energy range if the impurity concentration is sufficiently small. Note that if there were a continuum of distances between potentials, we should find a singularity only at the binding energy of a single well. Such

a singularity has, in fact, been observed for the model of independent, randomly scattered δ-functions (Lax and Phillips[27], Morrison[35]).*

It is not clear at present whether or not the density of states is mathematically well behaved in the regions of the energy spectrum where the histograms appear smooth.

In any region where $\rho(E)$ does not exist or is discontinuous, we expect $A(k,E)$ to be equally badly behaved. Like the cumulative density of states $N(E)$, the cumulative spectral density, formally defined by

$$N(k,E) = \int_{-\infty}^{E} A(k,E')dE', \tag{8.6}$$

will always exist and be continuous, but it need not be differentiable. In any physical experiment, of course, one always observes $\rho(E)$ or $A(k,E)$ averaged over a range of energies. To calculate these averages it suffices to know $N(E)$ and $N(k,E)$. Note that $N(k,E)$ can be approximated as accurately as desired, for a system that does not obey condition B, by calculating the function $N(k,E)$ for a second system, with a continuous random parameter, with a probability distribution peaked around the possible values of the discrete system. The function $N(k,E)$ for this second system can be obtained by numerical integration of eqn. 8.6, if one calculates $A(k,E')$ by the methods of section 6, at a closely spaced set of values of E'.

In any region where $A(k,E)$ is continuous, for a system with a discrete random parameter, it should be possible to obtain $A(k,E)$ directly by approximating the discrete distribution by a continuous one.

9. NUMERICAL CALCULATIONS

Numerical calculations of the cumulative density of states $N(E)$ have been carried out for a variety of one-dimensional

* It is interesting that the reasoning we have used to predict infinities in the density of states does not predict such singularities when applied to three-dimensional models. A detailed physical analysis of the behavior of the density of states near the impurity binding energy, in a crystal with a low concentration of impurities, has been given by Lifshitz[29].

models. The analytic procedure of Subsection 5C, in which one calculates the expected number of nodes per unit length in $\phi(x)$ from the probability distribution of z, has been employed by Frisch and Lloyd[15] for the model of randomly scattered δ-functions, by Agacy and Borland[2] for a binary alloy, and by Borland and Bird[7] for a model of a liquid. A similar calculation for the lattice vibrations of a chain of random mass has been done by Agacy[1]. In all these, the integral equation 5.14 was solved numerically. In addition there have been *purely* analytic studies of the density of states for the model of randomly scattered δ-functions in the limit of high energies (Borland[3]) and, for energies close to the impurity binding energy, in the limit of small impurity concentration (Morrison[35]). We have already mentioned the analytic results for this model in the high-density limit (*i.e.* for the white-Gaussian-noise potential, example 5, section 1). Schmidt[40] has studied the density of vibrational modes, in the vicinity of the frequency of an isolated light atom, for a chain with dilute light impurities.

Monte Carlo calculations of $N(E)$, in which one counts the nodes of the function $\phi(x)$ for a particular random chain of finite length, have been performed for binary alloys (James and Ginsbarg,[22] Landauer and Helland[25]) and for randomly scattered δ-functions (Lax and Phillips[27]). Similar calculations have been performed by Makinson and Roberts[31] for several models of δ-functions of constant strength and variable position: for a "solid" model preserving long-range order (example 3, Section 3) and for several "liquid" models with and without short-range correlations among the unit cells.

Dean has employed a Monte Carlo method to calculate the distribution of vibrational modes in various random chains[8–10] (Dean's formulation is actually slightly different than that in Section 5). Martin[33] has been able to generalize Dean's procedure so as to calculate the frequency distribution for a random chain with second-nearest-neighbor interactions (a system governed by a fourth-order difference equation).

The momentum-dependent spectral density $A(k,E)$ has thus far been calculated only for the white-Gaussian-noise model and for a model of a particle in a thermal deformation potential on a discrete lattice (Halperin[17]).

In many of the papers mentioned above, the results of various approximate theories are compared with the exact one-dimensional results. In addition, there have been papers in which new approximations, useful for three-dimensional problems, have been tested against *previously calculated* one-dimensional models. We mention, in this connection papers by Klauder[24], Kane[23], des Cloizeaux[12], and Halperin and Lax,[18] all of which are concerned with impurity problems. Roberts[38a] has compared an approximate theory of liquid metals with the Monte Carlo calculations by Makinson and Roberts.[31] Makinson and Roberts' "liquid" and "fluctuating solid" models have also been analyzed in a book by Gubanov.[16]

Comparisons of "exact" and "approximate" calculations of one-dimensional vibrational models may be found in Maradudin, Montroll, and Weiss.[32a]

The results of some representative numerical calculations may be found in Figs. 1–11.

10. ENERGY GAPS

Many physicists have been concerned with the question, "To what extent do the energy gaps, characteristic of crystalline semiconductors or insulators, persist in disordered alloys or liquids?" This question has been studied for a number of one-dimensional models.

An energy gap is defined as an *interval* of energy over which the density of states $\rho(E)$ vanishes completely, or equivalently, over which $N(E)$ is constant. In any finite chain there may be one or two energy states in the energy gap, due to end effects, but the number of states per unit length, in the energy gap, is zero for an infinite system.

We shall again suppose that the random potential can be broken up into a series of unit cells, each of which is characterized by one or more random parameters. We do *not* require that the probability distribution of the random parameter in each cell be independent of the values of the random parameters in all the other cells. We do require, however, that the range of *possible* values for the random parameter be independent of the values of the parameters in all the other cells. (We may say that such a

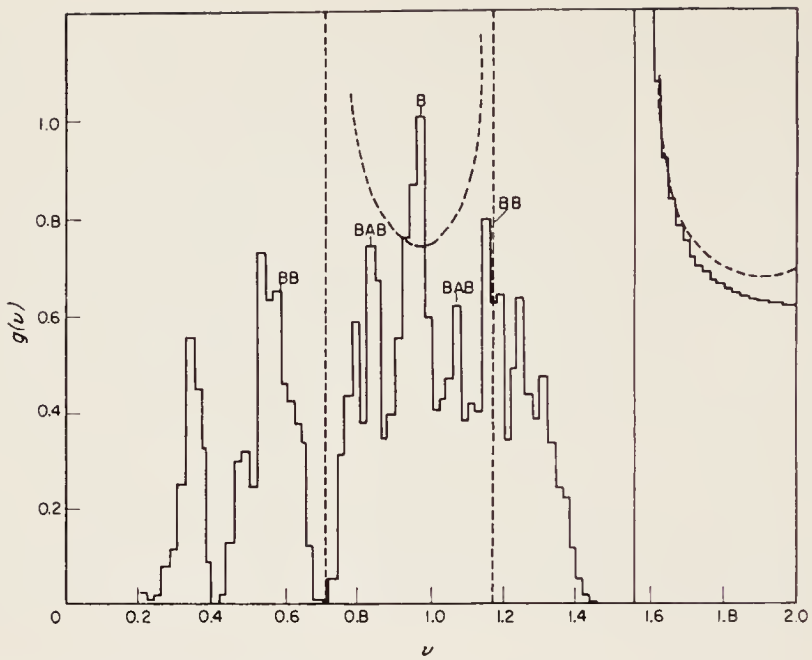

Fig. 1. Density of states histogram for an electron in a binary alloy (reproduced, by permission, from Agacy and Borland[2]). The solid curve gives the density of states histogram, $g(\nu) = 1/\Delta\nu$ times the number of energy states per unit length in the interval $\Delta\nu$, for a disordered alloy of two kinds of atom present in equal concentrations, computed by the analytic method of Subsection 5C. The broken curve represents the density of states for the corresponding ordered alloy . . . $ABABA$ . . . The atom A is represented by a δ-function with coefficient $u_A = -4$, atom B by a δ-function with coefficient $u_B = -0{\cdot}4$. The distance between successive δ-functions is a constant, which is chosen to be the unit of length. The unit of energy has also been chosen so that $\hbar^2/2m = 1$. The parameter ν is related to energy by $\nu = \frac{1}{2}E^{\frac{1}{2}}$.

For these parameters, a lattice of pure A would have an energy gap in the region $0 < \nu < \pi/2$, while pure B would have a gap for the smaller region $1{\cdot}504 < \nu < \pi/2$. The disordered lattice has an energy gap which coincides with that of pure B. Although it might appear from the graph above that the energy gap extends over a larger region than this, the density of states is not *exactly* zero outside of the gap of B.

Note the irregular behavior of the histogram for $\nu < 1{\cdot}4$. The peak labelled B coincides with the energy of the localized state of a B atom in a chain of pure A. The peaks labelled BB coincide with the bound states of a pair of adjacent B atoms in a lattice of A, and the peaks BAB correspond to two B atoms with one A atom in between.

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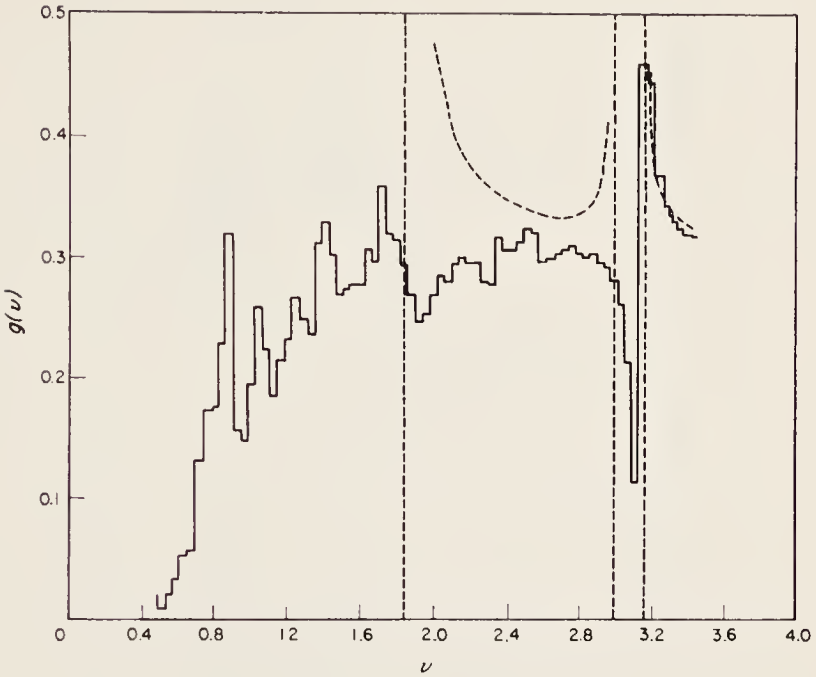

Fig. 2. Density of states histogram for an electron in a binary alloy (reproduced, by permission, from Agacy and Borland[2]). Same as Fig. 1, but for parameters $u_A = -2$, $u_B = +1$. In the present Figure the parameter ν is related to energy by $\nu = E^{\frac{1}{2}}$.

For these parameters, the lattice of pure A would have an energy gap for $2{\cdot}32 < \nu < \pi$. A lattice of pure B would have zero density of states for energies below $\nu = 0{\cdot}96$, and an energy gap for $\pi < \nu < 3{\cdot}50$. The disordered alloy has no energy gap.

As in Fig. 1, there is a region of irregular behavior in the density of states histogram. The peaks are, however, not so pronounced as in the former case.

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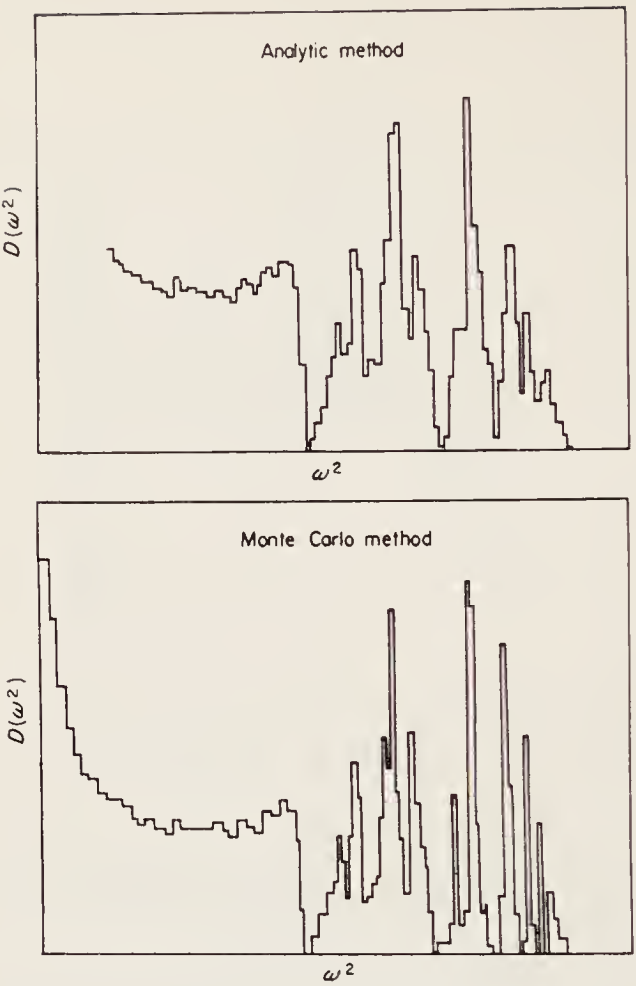

Fig. 3. Histogram of the vibration spectrum for a disordered "isotopic" two-component chain of mass ratio 2 : 1, with forces between nearest neighbors only. The ordinate $D(\omega^2)$ equals $1/\Delta\omega^2$ times the number of normal modes per atom in the interval $\Delta\omega^2$, where ω is the frequency. The upper curve was computed by Agacy[1] by numerical solution of an integral equation, according to the analytic method of Subsection 5C. The lower curve is the result of a Monte Carlo calculation by Dean, using a chain of 32,000 atoms. Irregular behavior of the density of states occurs in the frequency region forbidden to a pure lattice of heavy atoms, but allowed to a pure light lattice.

Reproduced, by permission, from P. Dean, *Lattice Dynamics*, Proc. Internat. Conference, Copenhagen, 1963, Pergamon Press, Oxford, 1964, p. 561.

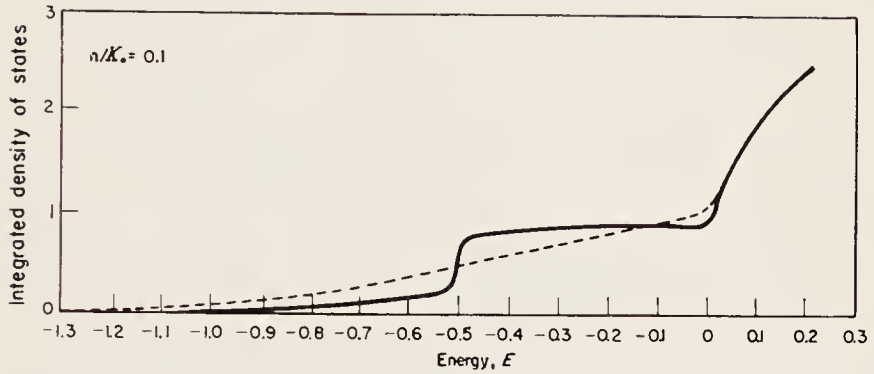

Fig. 4. Integrated density of states for a model of randomly scattered δ-functions (example 4, Section 3), case $n/\kappa_0 = 0{\cdot}1$ (low impurity density). Impurity atoms are represented by δ-functions with coefficient $-v_0 \equiv \hbar^2\kappa_0/m$, scattered independently on the line with an average density n per unit length. Energy is measured in terms of the energy unit $\hbar^2\kappa_0^2/m$. The ordinate gives the number of states per impurity atom, with eigenvalue less than given energy.

The solid curve is the exact integrated density of states as calculated by Frisch and Lloyd[15] using the analytic method described in Subsection 5C. The dotted curve is the result of "Approximation No. 5" of Klauder,[24] an approximation similar to the Brueckner approximation for Fermi liquids.

Reproduced, by permission, from Klauder.[24]

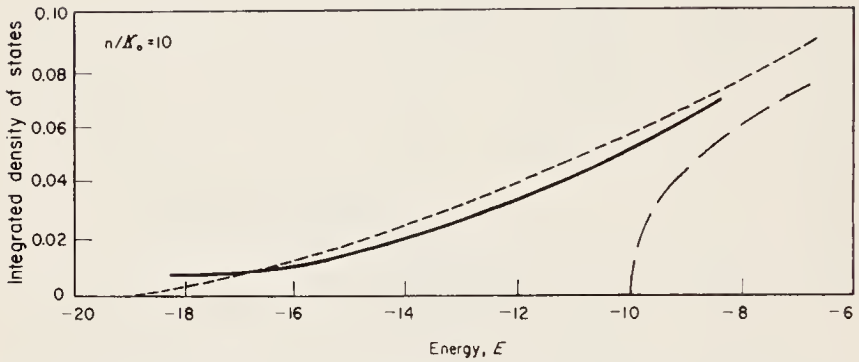

Fig. 5. Integrated density of states for randomly scattered δ-functions. Same as Fig. 4, but with $n/\kappa_0 = 10$ (high impurity density). The solid curve is the exact integrated density of states; the dotted curve is Klauder's "Approximation 5". The broken curve represents the density of states of a free electron in a uniform potential of value $-10\,\hbar^2\kappa_0/m$, equal to the average potential of the disordered system. The difference between the exact curve and the broken curve represents, in a sense, the effects of fluctuation about the mean potential.

Klauder's approximation appears to be better for high than for low impurity densities. It is not exact, however, even in the limit $n/\kappa_0 \to \infty$, where the fluctuations about the mean can be represented by white-Gaussian-noise.

Reproduced, by permission, from Klauder.[24]

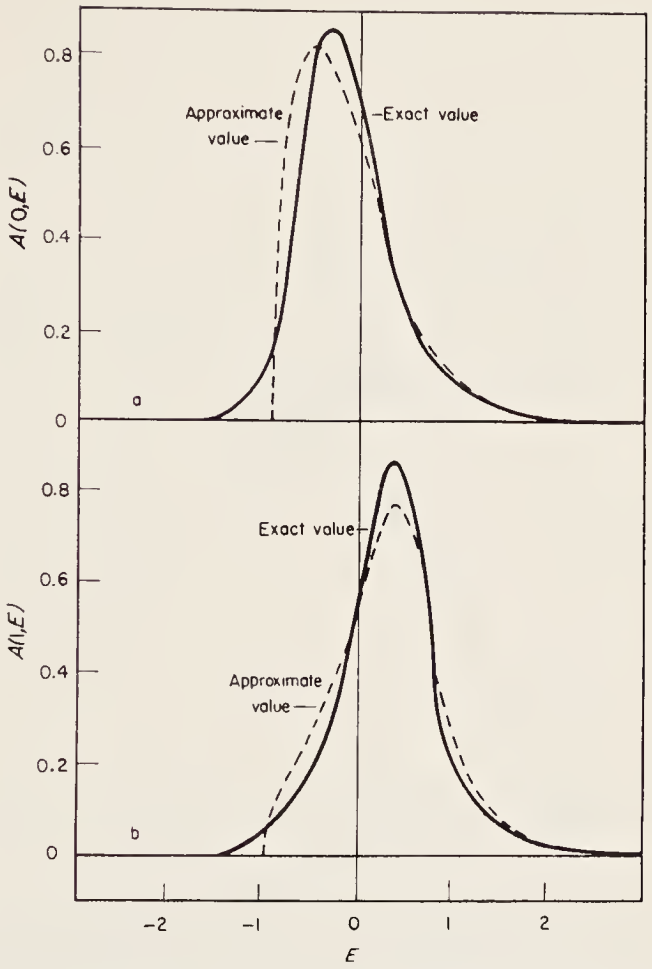

Fig. 6. Spectral density $A(k,E)$ for white-Gaussian-noise model, example 5, Section 3. (a) Wave number $k = 0$. (b) Wave number $k = 1$. Wave number is measured in terms of the unit of reciprocal length $k_0 = (Dm^2\hbar^{-4})^{\frac{1}{3}}$, where D is defined in Section 3; energy is measured in terms of the energy unit $E_0 = \hbar^2 k_0^2/m$, and the spectral density in units of E_0^{-1}. The exact curve has been calculated by Halperin[17] using the method described in Section 6; the approximate curves have been calculated by using either Approximation #5 or #3 of Klauder, the two approximations being equivalent in the limit of infinite impurity density.

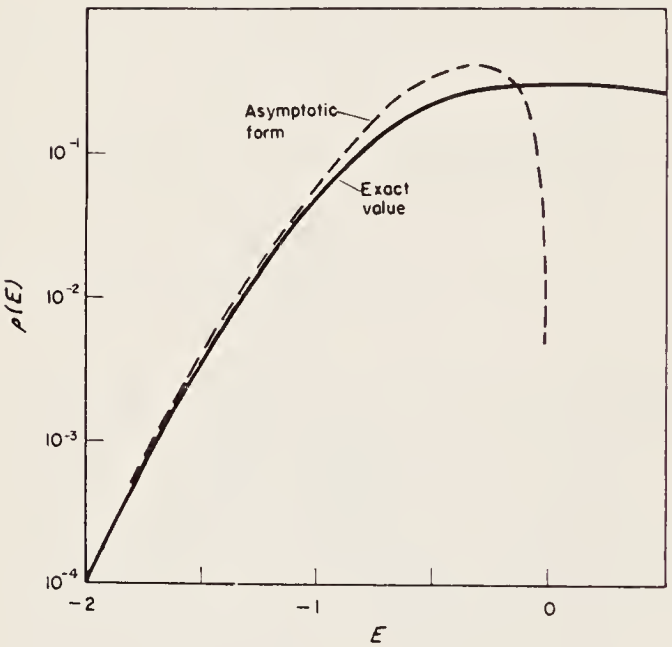

Fig. 7. Density of states $\rho(E)$ for white-Gaussian-noise model, compared with its asymptotic form for low energies, $\rho_{as}(E) = 8\pi^{-1}|E|$ exp $[-\frac{4}{3}|2E|^{\frac{3}{2}}]$. Energy is measured in units of E_0, density of states in units of $k_0 E_0^{-1}$, where k_0 and E_0 are defined in the caption of Fig. 6. The asymptotic form is predicted correctly by the approximate theories of Halperin and Lax[18] and of Zittartz and Langer.[41]

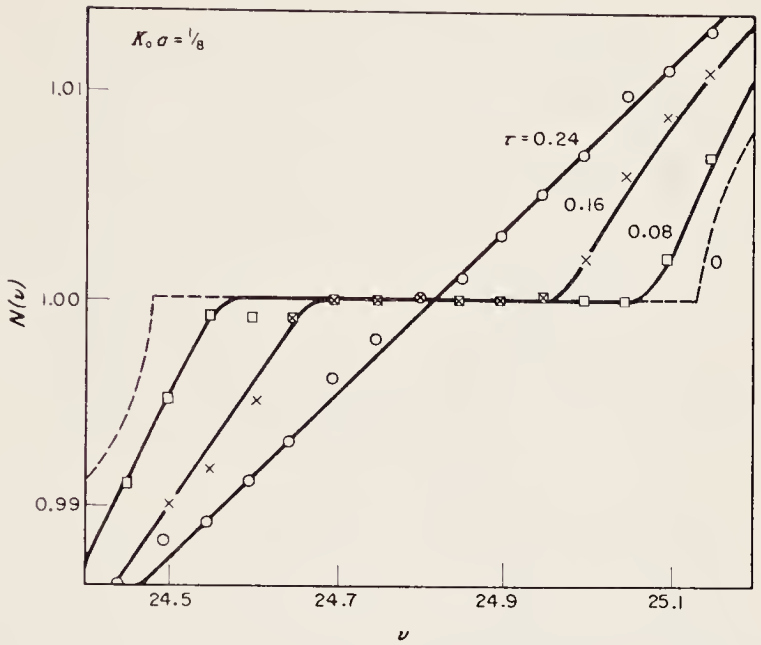

Fig. 8. Integrated density of states for a model of a solid with a long-range order and a short-range disorder (reproduced, by permission, from Makinson and Roberts[31]). The calculations have been performed by the Monte Carlo method (Subsection 5B) for a chain of 1,000 cells. The model is a special case of example 3, Section 3. The atomic potentials are δ-functions with coefficient $-v_0 = -\hbar^2\kappa_0/m$. The i'th δ-function is located at the point $(i \pm \tau)a$, where a is the "lattice constant," τ is a positive number smaller than $\frac{1}{2}$, and $+$ and $-$ signs occur randomly with equal probability. The quantity ν is related to energy by $\nu = (2mE)^{\frac{1}{2}}\hbar^{-1}\kappa_0^{-1}$. The ordinate gives the cumulative number of states in a length a. Represented here is a weak-binding case, $\kappa_0 a = \frac{1}{8}$, for energies near the first forbidden zone of the periodic lattice.

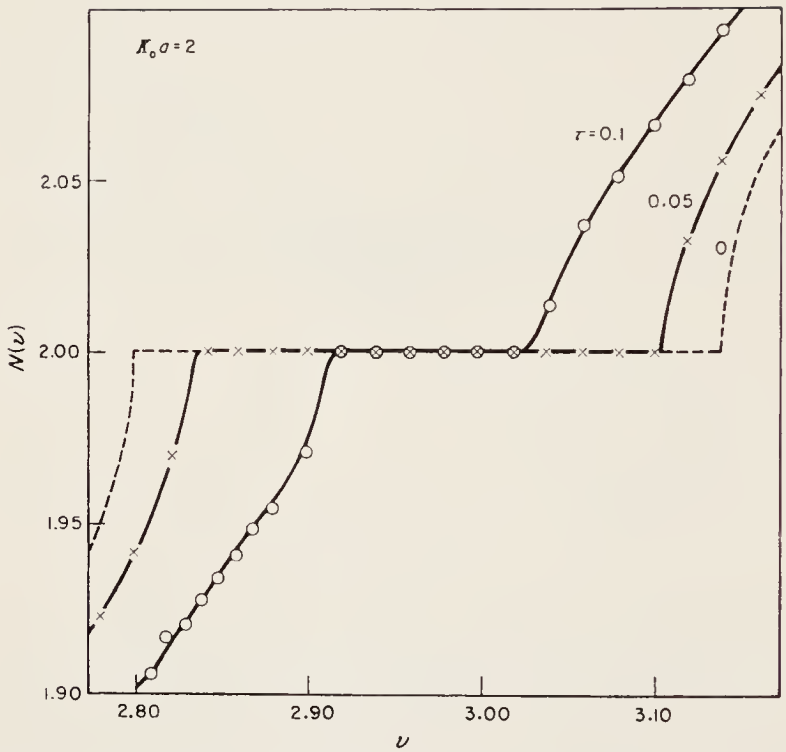

Fig. 9. Integrated density of states for a model with long-range order (reproduced, by permission, from Makinson and Roberts[31]). Same as Fig. 8, but for a tight-binding case, $\kappa_0 a = 2$. Energies are in the vicinity of the second forbidden zone of the periodic latice.

Makinson and Roberts' calculations indicate no qualitative difference between models with and without long-range order.

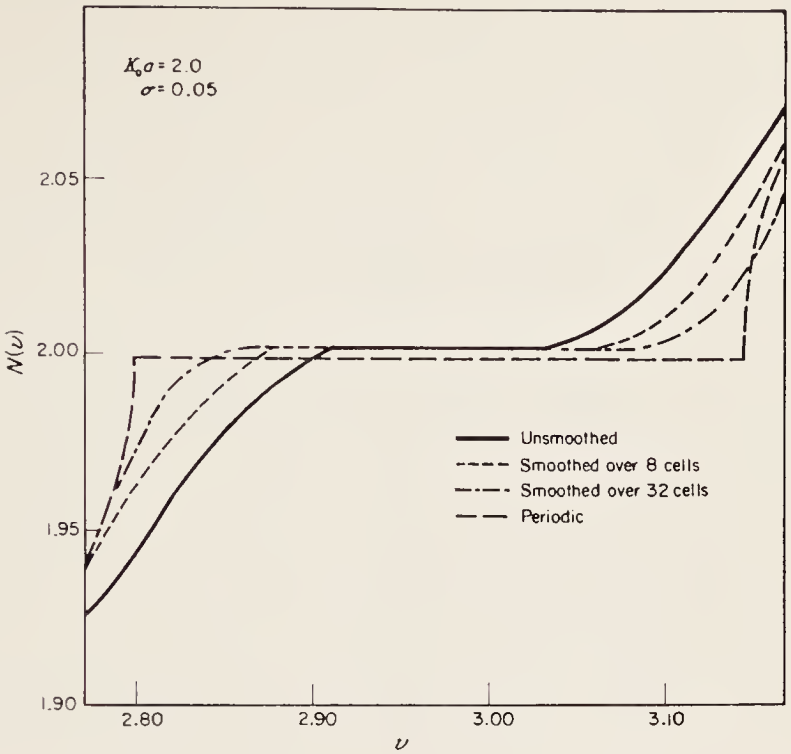

Fig. 10. Integrated density of states for liquid models with varying amounts of short-range order but no long-range order (reproduced, by permission, from Makinson and Roberts[31]). The unit cell consists of a δ-function with coefficient $-v_0 \equiv -\kappa_0\hbar^2/m$ followed by a region of potential zero and random length λ_i. For the "unsmoothed case," we have $\lambda_i = a\mu_i$, where a is the average lattice constant and the μ_i are independent random variables with a cut-off parabolic distribution of mean 1 and standard deviation σ:

$$p(\mu) = \frac{3\sqrt{5}}{20\sigma}\left[1 - \frac{(\mu-1)^2}{5\sigma^2}\right], \quad \text{for } |\mu - 1| \leqslant \sigma\sqrt{5},$$
$$= 0, \quad \text{for } |\mu - 1| > \sigma\sqrt{5}.$$

For the "smoothed cases" Makinson and Roberts have introduced correlations among the unit cells by choosing

$$\lambda_i = \frac{a}{M}\sum_{j=i}^{i+M-1}\mu_j,$$

where M is an integer greater than 1, and the μ_j are independent random variables, as before. Depicted here is the integrated density of states, per unit cell, for parameters $\kappa_0 a = 2$, $\sigma = 0{\cdot}05$, for smoothed cases with $M = 8$ and $M = 32$, for the unsmoothed case ($M = 1$), and for the periodic case ($M = \infty$). The energy parameter ν is the same as in Figs. 8 and 9. The region shown here includes the second forbidden band of the periodic lattice. Although on the basis of this Monte Carlo calculation there appear to be energy gaps for the disordered systems also, it can be shown that the density of states is non-zero for the disordered systems throughout the indicated energy

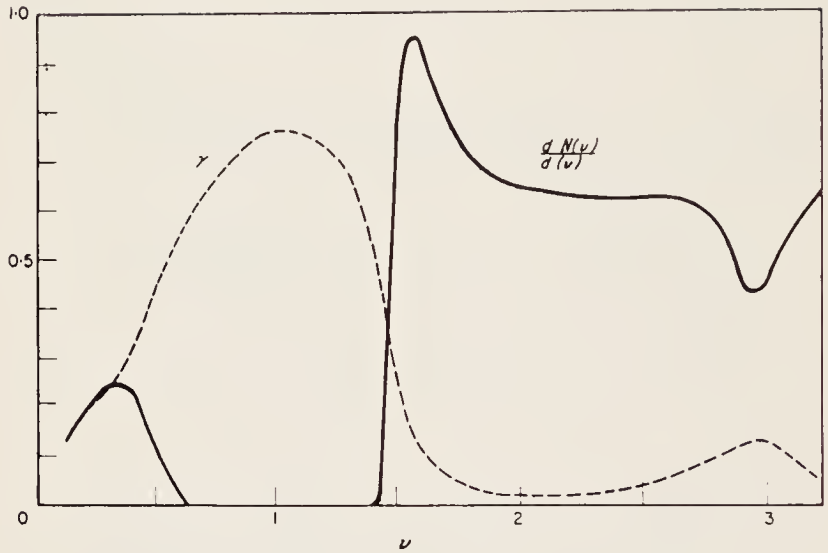

Fig. 11. Density of states and wavefunction-localization-constant γ, for a liquid model (Borland[5]). The unit cell consists of a δ-function with coefficient $-v_0 = -4$, followed by a region of potential zero and random length λ_i. The λ_i are independent and are uniformly distributed in the interval $(1 - \frac{1}{10}\sqrt{3}) < \lambda_i < (1 + \frac{1}{10}\sqrt{3})$. Units have been chosen such that $\hbar^2/2m = 1$. The abcissa ν is related to the energy by $\nu = \frac{1}{2}E^{\frac{1}{2}}$. The solid curve gives the density of states $dN/d\nu$, where $N(\nu)$ is the number of states per unit length with energy parameter less than ν. The broken curve gives wavefunction localization constant γ, defined in Section 11. The model has an energy gap in the region $0{\cdot}85 < \nu < 1{\cdot}34$.

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system has "limited correlations" among the unit cells.) In point of fact, whether or not an energy E lies in an energy gap depends solely on the range of possible unit cells and does not depend on the probability distribution over this range. We can easily derive a *necessary* condition for E to lie in an energy gap of a random potential with limited correlations.

Theorem: *The energy E cannot lie in an energy gap of the random system unless it falls in an energy gap for every periodic lattice whose unit cell is one of the possible unit cells of the random lattice.* The proof of this theorem is the following. We assume for simplicity that λ_i is a discrete parameter. Suppose that the energy E lies within an energy band of a periodic lattice with a unit cell characterized by the parameter $\lambda_i = \Lambda$. In a random lattice of infinite length there will be an infinite number of regions where we find n successive unit cells with $\lambda_i = \Lambda$, if n is any finite number, no matter how large. Let ε be any positive number. Then in each region of a sufficiently large number of successive unit cells, with $\lambda_i = \Lambda$, we can always construct a wave packet, $\psi(x)$, which vanishes outside the region, and such that

$$\int \psi(x)(H - E)^2\psi(x)dx < \tfrac{1}{2}\varepsilon^2. \tag{10.1}$$

If we expand the wave packets in terms of the eigenfunctions of the Hamiltonian, we find that there must be an infinite number of eigenfunctions whose energies differ from E by less than ε. Thus E cannot fall inside an energy gap of the random solid. (Note that the above proof is also applicable to three-dimensional models.)

To construct useful sufficient conditions for the existence of an energy gap is more difficult. The converse of the above theorem is, in general, not true: in some models there will be ranges of energy which are not forbidden to the random system, even though they fall within an energy gap for every corresponding period solid. (Any random potential of type 3, Section 3, will be an example of this.) There are some models, however, in which the energy gaps do coincide with the intersection of the energy gaps of the corresponding periodic potentials. For example, Luttinger[30] has shown this to be the case for any binary alloy in which the two kinds of atom are represented by δ-function

potentials of different strengths, with equal distances between the atoms.

Borland[4] has studied random potentials of the form of example 2, Section 3, wherein the unit cell consists of a given potential well, followed by an interval of zero potential and random length λ_i. The parameter λ_i is allowed to take on any value in an interval $[a,b]$. Borland has found a set of sufficient conditions for an energy E to lie in an energy gap of the random potential, expressed in terms of the minimum and maximum values of λ_i. (Similar conditions were found independently by Makinson and Roberts[32,39].) In fact, it can be shown that Borland's conditions just correspond to the requirement that E lie in the energy gap for every periodic lattice with $a \leqslant \lambda \leqslant b$ (Hori[19]). These results can be trivially generalized to the case where the range of λ_i is a set of several disjoint intervals. We therefore find, that for any type 2 model, as for Luttinger's model, a *sufficient* as well as necessary condition for E to lie in an energy gap of the random system is that E be in the energy gap of every corresponding periodic lattice.

Dworin[13] has studied random potentials with unit cells that are symmetric but otherwise arbitrary and has derived a number of useful sufficiency conditions for energy gaps. It is not sufficient, in this general case, that E be in the energy gap for every corresponding periodic solid. It is not known whether Dworin's conditions are necessary as well as sufficient.

Most of the attempts to find sufficiency conditions for the existence of energy gaps have proceeded as follows. One attempts to divide the line $-\infty < z \leqslant +\infty$ into two proper sub-sets A and B, such that for all energies in a neighborhood of E, no matter what the value of λ_i, we automatically find $z(x_i)$ in A whenever $z(x_{i-1})$ is in A. If one can find such a division it follows that E lies in an energy gap; for, if one chooses as boundary conditions a value of Z_0 which lies in A and a value of Z_L which lies in B, then clearly no eigenvalues can occur in the neighborhood of E.

Examples of systems with energy gaps may be found in Figs. 1 and 11. The disordered systems in Fig. 10 do *not* have true energy gaps in the represented energy range, despite the fact that the density of states is so small in part of this range that no state may be found in a Monte Carlo chain of a few thousand cells.

Several authors have applied approximate methods to the

study of energy gaps in one-dimensional systems and have found results in conflict with the rigorous results presented above (Edwards,[14a] Hiroike[18a]). Although the approximations employed by these authors may be adequate for many purposes, they are not adequate for deciding whether or not the density of states is exactly zero in a given region.

11. LOCALIZATION OF WAVE FUNCTIONS

In 1961, Mott and Twose[36] conjectured that essentially all the energy eigenfunctions in an infinitely long one-dimensional random potential are localized in space. Makinson and Roberts[32] gave some further support to this proposition with arguments that wave functions must be localized at least in the neighborhood of any energy gaps.

Later a rigorous argument was given by Borland[5] for the exponential localization of eigenfunctions at all energies in certain kinds of random potentials. The potentials considered by Borland are general potentials of the form of example 2, Section 3: potential wells of fixed shape with statistically independent separations between neighboring wells.

What Borland has actually shown is that in any given energy range the expectation value of the fraction of eigenstates that are not localized must approach zero as the length of the system approaches infinity. It is possible, of course, to make much stronger conjectures. For example, it may be true that the expectation value of the *number* of non-localized eigenstates tends to zero as the length of the system increases (and that therefore, for sufficiently large N, almost every member of the ensemble of possible potentials will have no non-localized eigenstates in the energy range). However, this stronger statement has not been proved.

We must also make somewhat more precise the meaning of "exponential localization". It is convenient to define the amplitude $A(x)$ of a wave function $\psi(x)$ by

$$A(x) = [\psi(x)^2 + \psi'(x)^2]^{\frac{1}{2}}. \tag{11.1}$$

(This definition of amplitude is actually slightly different than Borland's, but the difference is unimportant.) The amplitude

$A(x)$ will never be zero, since the wave function and its derivative cannot vanish simultaneously.

$A(x)$ will generally have a maximum at some point x_0 on the line. If the energy eigenfunctions in a neighborhood of a certain energy E are exponentially localized, then there exists a number $\gamma > 0$, independent of the length of the system, such that for wave functions in the vicinity of energy E, the function $A(x)$ behaves like $A(x_0) \exp(-\gamma|x - x_0|)$. The value of $A(x)$ may, of course, fluctuate about this "average behavior", but Borland's definition of localization requires that, for all x in a large system,

$$|\log \{A(x_0) \exp(-\gamma|x - x_0|)/A(x)\}| \ll \gamma L. \tag{11.2}$$

Again, a number of somewhat stronger definitions of localization are possible, but a rigorous proof of localization under a stronger definition has not been given.

Borland's proof of the localization of wave functions has not been universally accepted as valid by workers in the field. The proof is rather long and complicated, and a number of details have been omitted from the published results. Nonetheless, a careful examination of Borland's proof confirms that each step can be rigorously justified. We can give here only an outline of the argument.

Step 1: The first step is to show that the wave function $\phi(x)$, whose logarithmic derivative is fixed at $x = 0$, increases exponentially, with probability 1, as $x \to \infty$. This result is at first glance rather surprising and deserves a few words of discussion. We know that there is no fundamental asymmetry between left and right and we wonder why the wave function should always increase as we move to the right. The resolution of this paradox is not difficult. In general, in a long random potential, there will be two independent solutions of the Shrödinger equation, one of which is exponentially decreasing to the right and while the other is exponentially increasing to the right.* If we select an arbitrary

* We may define the *pure* increasing function as that solution for which the ratio $A(x_N)/A(0)$ is a maximum, the pure decreasing function as that for which the ratio is minimum. It can be shown that in *any* potential, the maximum value of this ratio is the reciprocal of the minimum. It follows immediately that if there is a decreasing function there will also be an increasing function.

value for the logarithmic derivative $z(x)$ at $x = 0$, we shall usually designate a linear combination of these two solutions, with coefficients such that the amplitudes of the two components will have equal orders of magnitude at $x = 0$. If we now let x become very large the exponentially decreasing solution disappears and the exponentially increasing component remains. We shall have an exponentially decreasing solution only if $z(0)$ is selected to lie in an extremely narrow range about the value of $z(0)$ for the pure decreasing solution. We also note that for any choice of $z(0)$ such that we have an exponentially increasing function, the value of $z(x_N)$ will approximately equal that for the pure increasing function, essentially independently of $z(0)$.

It is easy to see that the reverse of the above arguments applies if we arbitrarily choose the value of $z(x)$ at x_N instead of at zero. In that case, the amplitude of the wave function will almost always increase when x moves to the left.

The rate at which the amplitude $A(x)$ increases, for the exponentially increasing solutions, can be calculated if the limiting probability distribution $P(z)$ is known. Let $r(z,\lambda)$ be the value of $\log [A(x_i)/A(x_{i-1})]$ that occurs if $z(x_{i-1})$ has the value z and λ_i has the value λ. The expectation value of $r(z,\lambda)$ is given by

$$\langle r \rangle = \int r(z,\lambda) P(z) p(\lambda) d\lambda dz \equiv \gamma \bar{l}. \tag{11.3}$$

The net increase in $\log A(x)$, for a long chain, will therefore be approximately

$$N\gamma\bar{l} = \gamma \langle L \rangle \tag{11.4}$$

for almost all cases; deviations from this expected increase will generally be of order $N^{\frac{1}{2}}$.

If it is true that there is in general an exponentially increasing solution and an exponentionally decreasing solution of the Shrödinger equation, then the solution $\phi(x)$ whose logarithmic derivative is specified at $x = 0$ will be exponentially increasing, and γ will be greater than zero.

However, we have not yet disproved the possibility of there being neither an increasing nor a decreasing solution, that is, of $\gamma = 0$. Borland and others have, in fact, calculated γ for a number of models, according to eqn. 11.3, and found that $\gamma > 0$. However, it is clearly desirable to have a general proof that

$\gamma \neq 0$. Toward this end Borland has proved the following theorem:

Step 1a. The constant γ will equal zero if, and only if, the limiting probability distribution of the logarithmic derivative is the same when the initial value of the logarithmic derivative is specified at $x = 0$ as when it is specified at x_N. That is, $\gamma = 0$ if and only if

$$P(z) = g(z). \tag{11.5}$$

It should be remarked that the "ergodic hypothesis" invoked by Borland in this step can be rigorously proved, without much difficulty.

Step 1b. Borland shows that $P(z)$ does not equal $g(z)$ for a general potential of the type 2, Section 3 (fixed potential wells with variable distance between the wells). Borland's proof breaks down only at certain isolated energies, for certain special potentials, where, in fact, we do find $\gamma = 0$. It can also be shown that $P(z)$ does not equal $g(z)$ for a number of models of type 1, Section 3, and for the Gaussian-white-noise model (example **5**, Section 3). A proof for the most general kinds of random potentials has not yet been found. Nonetheless, it seems almost certain that $P(z)$ does not equal $g(z)$, except at some isolated energies, for any potential satisfying conditions A and B. It is probable that $P(z) \neq g(z)$ even for potentials which do not satisfy conditions A and B.

Let us emphasize that even when the expectation value $\gamma \bar{l}$ is greater than zero, it only follows that there will be an increasing and a decreasing solution of the Schrödinger equation *almost* all of the time. The "almost" is an important qualification, because, as we shall see, the exceptions occur just when E is an eigenvalue of the potential.

Step 2. Let us now consider the behavior of the logarithmic derivative $z(x)$ as a function of the energy E when $z(0)$ is held fixed. We assume that x is a large distance from the origin. It can be shown that, in general, $z(x)$ changes slowly with energy, but that in the vicinity of certain special energies, $z(x)$ is changing very rapidly. Let us suppose that the value of $z(x)$ in the region of slow change immediately preceding a certain region of rapid change has the value ξ. Then we find that as E increases through

the region of rapid change, $z(x)$ drops from ξ to $-\infty$, jumps to $+\infty$, and then drops down again to approximately the same value ξ. Thus the value of $z(x)$ passes through all values from $+\infty$ to $-\infty$ in a very small energy interval. It can be shown that almost all the change in z occurs in these small energy intervals.

If the point x were at the right-hand end of the system, then the intervals of rapid change would occur at the energy eigenvalues of the system, since the value of $z(x)$ will pass through the required boundary value Z_L once in each such energy interval. The energy eigenvalues would occur at random places, depending on the particular potential configuration between 0 and x. The average number of eigenvalues, and hence the number of regions of rapid variation of $z(x)$, which occur in the energy interval $(E,E + \Delta E)$, must be equal to $x\rho(E)\Delta E$, where $\rho(E)$ is the number of eigenstates per unit energy and per unit length for a very large system. Let us note that, because the regions of rapid variation of z form only a very small part of the total energy interval ΔE, and because these special regions depend on the potential between 0 and x, it is no longer possible to assert that $A(x)$ will almost always be very much greater than $A(0)$, if the energy is known to be in such a special region.

Step 3. If x is not at the right-hand end of the system, we must consider the logarithmic derivative at point x, of the solution of the Schrödinger equation satisfying the boundary condition at x_N. Let us denote this logarithmic derivative by $y(x)$. Like $z(x)$, the value of $y(x)$ will be almost independent of energy except in certain narrow energy regions where it passes through all values from $-\infty$ to ∞. The expected number of such regions, in the energy interval $(E,E + \Delta E)$ will be $(L - x)\rho(E)\Delta E$.

Energy eigenvalues of the entire system occur at energies where $z(x) = y(x)$. It is clear that one eigenvalue must occur in each region of rapid change of either $z(x)$ or $y(x)$. A fraction $(L - x)/L$ of the eigenvalues will occur because of rapid change in $y(x)$. The energies at which $y(x)$ changes do not depend in any way on the potential between 0 and x. Thus the arguments of step 1 are unaffected for these eigenvalues, and the amplitude of the wavefunction will almost certainly increase exponentially between 0 and x. Similarly, for a fraction x/L of the eigenvalues, the wavefunctions increase as we move from x_N to x.

Step 4. Every eigenfunction will have a point x_m such that the amplitude of the wave function increases exponentially from $x = 0$ to $x = x_m$, and ceases to increase exponentially at x_m. Similarly there will be a point x_M, such that the wave function decreases exponentially between x_M and L, but does not exhibit this behavior in the region $x < x_M$. From the results of step 3 it can be shown that the value of $(x_M - x_m)/L \approx 0$ for almost all eigenfunctions, and therefore almost all the eigenfunctions are exponentially localized.

The only step in Borland's proof which depends critically on the nature of the random potential is step 1*b*. If it can be shown, for a particular random potential satisfying condition B, that $P(z) \neq g(z)$, then it can be shown that the eigenstates are exponentially localized, regardless of whether or not each unit cell is statistically independent of all the others (condition A). Of course, we can no longer calculate γ from eqn. 11.3 if condition A is violated, nor can we find $P(z)$ from eqn. 5.14.

For a potential violating condition B, i.e., for a unit cell with a discrete random parameter, the situation is somewhat less clear. Although steps 1*a*, 2, and 4 can be made rigorous after slight modifications, there appears to be some difficulty with step 3. Dean and Bacon[11] have calculated the normal modes of a random chain of 50 atoms with two kinds of mass and have found that the eigenstates are in fact localized, except at the limit of zero frequency. For those classes of random potentials for which Borland's proof is valid, the eigenstates are localized no matter how small the degree of disorder and no matter what the energy E (except possibly for certain isolated energies). It should be remembered, however, that even if the eigenfunctions in a one-dimensional random model are always localized, the localization constant may depend greatly on the value of the energy and on the amount of disorder. Quantitative calculations of γ, for various models, may be found in Agacy,[1] Agacy and Borland,[2] and Borland and Bird,[7] as well as in the original paper of Borland[5] (see Fig. 11).

A constant γ may be calculated from eqn. 11.3 even if the energy E falls within an energy gap of the random system. The significance of γ in such a case is the following: If a new kind of impurity or point defect is added to the random system, that can

create a bound state at energy E, then this bound state will decay exponentially away from its center with decay constant γ.

12. ABSENCE OF D.C. CONDUCTIVITY

The localization of wave functions discussed in the previous Section has an important implication for the d.c. conductivity. It has been argued that the d.c. conductivity for a set of non-interacting electrons in a static, random potential will vanish completely whenever the energy eigenfunctions, in a neighborhood of the Fermi energy, are all localized in space (Mott and Twose[36]). If we accept this proposition, we are forced to conclude that in many, if not all, one-dimensional models there is zero d.c. conductivity, no matter how small the amount of disorder. This is a remarkable result, because it is in direct contradiction to transport theory or perturbation theory, both of which predict a finite, non-zero, d.c. conductivity whenever the Fermi energy does not lie within an energy gap, if the disorder is sufficiently small.*

It would be very interesting to confirm the absence of d.c. conductivity, in one-dimensional random potentials which obey conditions A and B, by use of the procedure described in Section 6 for calculating the function $F(E,E')$. If we study eqn. 2.15 in the limit $\omega \to 0$, we find that

$$\sigma(0) = \frac{\hbar\pi e^2}{m^2} \int_{-\infty}^{\infty} \frac{-df(E)}{dE} F(E,E^+)dE, \tag{12.1}$$

where

$$F(E,E^+) = \lim_{\omega \to 0} F(E,E + \hbar\omega), \tag{12.2}$$

* It can be shown rigorously that the d.c. conductivity vanishes if the eigenfunctions with energy near the Fermi energy are localized in the following sense: that the expectation value of $\int \psi_j(x)^2 (x - x_j)^2 dx$ is finite in the limit $L \to \infty$, where x_j is the center of gravity of the squared wavefunction $\psi_j(x)^2$. The localization established by Borland's arguments, as outlined in Section II, is stronger in one respect than the above definition: Borland shows that the wavefunctions fall off *exponentially* away from the central region where the wavefunction is large. The localization established by Borland's argument is, however, not sufficient rigorously to establish vanishing d.c. conductivity, because although it is established that the width of the central region is infinitesimal compared to L when $L \to \infty$, it is not established that this width actually remains finite. Further details will be published in a future paper.

and $F(E,E+\hbar\omega)$ is defined by eqn. 2.16 taken in the limit of an infinite system. It is important to take the limit $L \to \infty$ before the limit $\omega \to 0$, because $F(E,E)$ is equal to zero for any finite system. (This is just the trival result that the d.c. conductivity is zero in a finite system with reflecting boundary conditions.)

At absolute zero temperature, the derivative of the Fermi function in eqn. 12.3 is simply a delta function at the Fermi energy, E_F. Thus, at absolute zero

$$\sigma(0) = \frac{\hbar\pi e^2}{m^2} F(E_F,E_F^+). \tag{12.3}$$

At finite temperatures $-(df/dE)$ is peaked about E_F, with a width of order k_BT, and a total area of unity. The value of the conductivity is thus an average of the zero-temperature conductivity over a range of Fermi levels (provided that the random potential is not itself temperature-dependent). The d.c. conductivity will vanish at all Fermi levels and all temperatures if, and only if, $F(E,E^+) = 0$ for all E.

It should be emphasized that in our models there are no phonons or other energy sources that can permit electrons to jump from one eigenstate to another without conservation of energy. If phonons of finite energy were included in any of our one-dimensional models, the models would not be exactly soluble by any known method and we cannot say positively what would be the resulting effect on the conductivity. Presumably, however, one would find a non-zero conductivity at finite temperatures (Mott and Twose[36]).

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APPENDIX

Convergence of the Probability Distributions $P_i(z)$

We state, without proof, a simple set of conditions which rigorously guarantee convergence of the probability distributions $P_i(z)$ to a continuous limiting distribution $P(z)$. We shall consider a unit cell that depends on a single continuous random parameter λ. (We may also include a discrete parameter η provided that η has a finite number of possible values and that the following conditions are satisfied for each value of η.) We assume that the probability distribution $p(\lambda)$ is a bounded piecewise-continuous function of λ.

1. We require that the random potential in the unit cell be a continuously differentiable function of λ. [If there are any finite jumps or δ-function singularities in $V(x)$, then we require that the magnitudes and positions of these singularities be continuously differentiable functions of λ.] If the length of the cell depends upon λ, it too must be continuously differentiable.

2. We shall assume that there is a finite upper limit to the length of the unit cell and to the magnitude of the potential in the cell (or to the magnitude of any δ-function singularities). We may then assume, with very little further restriction, that the range of the parameter is the closed interval [0,1].

3. Our final requirement is somewhat more complex and necessitates a few definitions. We shall say that a function $f(\lambda)$ is "stationary" at $\lambda = \lambda_0$ if the derivative of f is zero at λ_0. We shall say that $f(\lambda)$ is "strongly stationary" at λ_0 if $|f(\lambda) - f(\lambda_0)|$ decreases faster than any power of $|\lambda - \lambda_0|$, on an infinite sequence of points converging to λ_0. We shall define a stationary point of the transfer matrix $\mathbf{M}(\lambda)$, connecting the wave function and its derivative at x_i with their values at x_{i-1}, in a more complicated way. If $\operatorname{tr} \mathbf{M}(\lambda_0) \geqslant 2$, then we shall say that $\mathbf{M}$ is stationary at λ_0 if *either* of its eigenvectors is stationary at λ_0. If $\operatorname{tr} \mathbf{M}(\lambda_0) < 2$, we shall say that $\mathbf{M}$ is stationary at λ_0 only if all four components of $\mathbf{M}$ are stationary at λ_0. [The trace of $\mathbf{M}(\lambda_0)$ will be greater than 2 if, and only if, the energy E is within an energy gap of a periodic lattice with unit cell λ_0.] We define a strongly stationary point of $\mathbf{M}$ in a similar fashion, requiring the eigenvector, or the four components of $\mathbf{M}$, to be strongly stationary. Finally, our third condition for

convergence is that **M** have no strongly stationary points, and at most a finite number of stationary points, in the closed interval $0 \leqslant \lambda \leqslant 1$.

Any model satisfying these three conditions, at a given energy E, will have a continuous limiting probability distribution $P(z)$, at the given energy. It appears highly probable that any model satisfying conditions 1 and 2 will also satisfy condition 3, except possibly at certain isolated special energies, provided that the "unit cell" itself is not stationary with respect to λ. No proof of this has, however, been found.

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ELECTROCHROMISM

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INTRODUCTION

The term "electrochromism" has been proposed by Platt[1] to designate all changes in optical absorption or emission spectra of molecules in the condensed phase due to an external electric field. Although related to the Stark effect, the splitting in an electric field of the spectral lines of atoms and small molecules in the gas phase, electrochromism deals with unresolved spectra of relatively large molecules, such as aromatic compounds, in solution or in the crystalline state, and hence gets its separate meaning. Most of the work done so far in this field concerns ultraviolet and visible spectra. No visible colour change has been achieved up to the present in external electric fields. Nevertheless, the small measurable effects are meaningful for evaluating the absolute direction of transition moments, as well as of the dipole moments and polarizabilities of electronically excited states. Furthermore, these effects may help considerably in understanding the large solvatochromic shifts in the spectra of molecules in solution, as a special case of intrinsic electrochromism in the reaction field of the solvent.

In this review we first try to establish the connection between the Stark effect and electrochromism. This yields a justification for the approximations adopted in the theories of the latter. In subsequent chapters, experimental features and some applications will be discussed.

I. FREE MOLECULES IN AN ELECTRIC FIELD

A. Small Molecules

As long as the perturbation by the applied field is small compared with the separation of rotational states, spectral lines may still be assigned to the transition between zero field states of the free molecule. In this case, perturbation theory will lead to correct predictions concerning line shift and intensity change in terms of the dipole moment and polarizability of the excited state. Small molecules in moderately strong electric fields may be treated in this manner.

The theory of the Stark effect in pure rotational spectra may best be taken from the monograph by Townes and Schawlow.[2] It has been improved by Wharton and Klemperer[3] and adapted to rovibronic transitions by Freeman and Klemperer,[4] who determined dipole moments of the $n - \pi^*$ excited states of formaldehyde and propynal. Dows and Buckingham[5] discuss the possibilities of getting excited-state dipole moments of diatomic molecules from the intensities of field-induced lines.

However, for reasons to be set out in the next Section, investigations on the Stark effect of rotational lines are not well suited as a basis for the study of electrochromic effects of larger molecules.

B. Medium and Large Molecules

Molecules of medium size, with a molecular weight of about 200, have moments of inertia of the order of magnitude of some 10^{-38} g cm^2. The spacing between rotational levels is then comparable with the electric perturbation energy, even in relatively weak external fields. Thus an approximation starting from rotational states of the free molecule will no longer be appropriate. At the same time, provided that the temperature is not too low,

the number of molecules in high rotational states becomes so large that the orientation with respect to the field direction is more or less continuous.

The field-induced energy Δ_x in a state x consists principally of a first-order term Δ'_x and a second-order term Δ''_x . Δ'_x is simply $\boldsymbol{\mu}_x\mathbf{F}$ ($\boldsymbol{\mu}_x$ = dipole moment in state x, $\mathbf{F}$ = electric field). Δ''_x depends on the mixing of different rovibronic states. It arises from the same matrix elements [cf. eqn. (2)] that determine optical-transition probabilities and thus is most easily discussed with reference to the well-known optical selection rules.[6]

Thus, within the same vibronic state, a given rotational sublevel interacts only with neighbouring rotational sublevels. Measurements are usually taken with a spectral bandwidth large compared with both the spacing of adjacent rotational levels and the perturbation energy. Then for an electronic transition from any other state the mean transition energy and the total transition probability within the bandwidth will not change appreciably owing to this type of mixing.

Interaction of a rotational sublevel of a vibrational state with a rotational sublevel of another vibrational state of the same electronic state may be discussed starting from infrared selection rules. The infrared transition moments are relatively weak. A rotational state in an electric field gets small contributions from a few rotational states in the next higher, and from a few rotational states in the next lower, vibrational level. As the perturbing states lie nearly symmetrically to the perturbed one, and the matrix elements are of approximately the same magnitude, no significant energy shift is to be expected, except for the rotational levels in the zero vibrational state of each electronic level. Since absorption usually starts from the zero vibrational levels of the ground state, and the deformation of the molecule upon excitation allows transitions to higher vibrational levels of an upper electronic state, a shift of all but the zero-zero transition should be expected. The order of magnitude of this shift in a field of 10^5 v/cm is 3×10^{-5} cm^{-1} if a representative transition moment of 0·1 Debye and vibrational frequency of 3×10^{13} sec^{-1} are assumed.

Allowed transitions between different electronic states have moments of some Debyes. In spite of the larger energy difference

between interacting states, the energy shift due to the mixing of electronic states at the same field strength will, in general, be of the order of some 10^{-4} cm^{-1}. This determines the magnitude of second-order shifts in optical transitions.

Now first-order shifts in optical transitions, Δ'_x, $-\Delta'_x = (\boldsymbol{\mu}_x, -\boldsymbol{\mu}_x)\mathbf{F}$, are of the order of magnitude of 2 cm^{-1} [$(\boldsymbol{\mu}_x, -\boldsymbol{\mu}_x) =$ 1 D; $F = 10^5$ v/cm]. However, owing to the nearly isotropic orientation, only a small fraction of this shift, namely $\boldsymbol{\mu}_x\mathbf{F}/kT \approx 10^{-2}$ at room temperature, will appear in the spectrum, as will be shown. Second-order shifts, depending on $|\mathbf{F}|^2$, will not average out so much. Nevertheless, for molecules with not too small dipole moments, the first-order perturbation will predominate. It depends on the difference between the dipole moment of the initial and the final state, and it will not differ much for different transitions within a given band since the dipole moments in different rotational and vibrational sub-states of the same electronic state are approximately equal. Within second-order effects the interaction between different electronic states has been shown to be the most important one.

It thus seems a reasonable approximation to assume that in an electric field the contour of an electronic absorption band, when measured with a spectral bandwidth large compared with the perturbation energy ($\approx$2 cm^{-1}), is shifted in wave number as a whole and that the extinction coefficient changes by the same factor throughout the band. Various theories have been stated along these or similar lines in the last years,[7–12] the most elaborate and most recent version being due to Liptay.[13]

If, for the reasons just stated, only interactions between different electronic states are considered, perturbation theory may be applied. The perturbation is described by the Hamiltonian

$$\mathscr{H} = -\tilde{\mathbf{F}}\boldsymbol{\mu}, \tag{1}$$

where $\tilde{\mathbf{F}}$ is the (row-)vector of the homogeneous static external electric field and $\boldsymbol{\mu}$ is the (column-)vector operator of the dipole moment.

The perturbation matrix element

$$H_{ik} = \langle \psi_i^0 | \mathscr{H} | \psi_k^0 \rangle = -\tilde{\mathbf{F}}\boldsymbol{\mu}_{ik} \tag{2}$$

is then equal to the dipole energy of state i in the field, if $i = k$, or

equal to the scalar product of the field strength with the transition moment of the transition $i \rightarrow k$ if $i \neq k$.

The energy change of state i in the field may be written

$$\Delta E_i = -\tilde{\mathbf{F}}\boldsymbol{\mu}_i - \tfrac{1}{2}\tilde{\mathbf{F}} \sum_{k \neq i} \frac{2\boldsymbol{\mu}_{ik}\tilde{\boldsymbol{\mu}}_{ki}}{E_k^0 - E_i^0} \cdot \mathbf{F}, \tag{3}$$

where

$$\sum_{k \neq i} \frac{2\boldsymbol{\mu}_{ik}\tilde{\boldsymbol{\mu}}_{ki}}{E_k^0 - E_i^0}$$

yields the polarizability tensor of the molecule. Since ΔE_i depends on the orientation of the molecule with respect to the field, a first field effect consists at non-zero temperature of a partial alignment of the molecules. Consequently the sample will exhibit dichroism.

Another electronic state f will show a different energy shift ΔE_f, depending on its dipole moment and polarizability and the molecular orientation. A transition from state i to state f will then undergo a shift in wavenumber:

$$\Delta\tilde{\nu}_{if} = \frac{1}{hc}(\Delta E_f - \Delta E_i). \tag{4}$$

In accordance with our assumptions, this shift is believed to be the same for any transition between rotational or vibrational sublevels of the electronic states i and f. It must be understood as the mean shift of individual lines.

A third influence of the electric field is a change in the direction and magnitude of transition moments. Second-order perturbation theory yields for the wave function of a state i:

$$\psi_i = \psi_i^0 + \tilde{\mathbf{F}} \sum_k \frac{\boldsymbol{\mu}_{ik}}{E_k^0 - E_i^0} \psi_k^0 + \tilde{\mathbf{F}} \sum_{k \neq i} \sum_{j \neq i} \frac{\boldsymbol{\mu}_{ji}(\tilde{\boldsymbol{\mu}}_{kj} - \tilde{\boldsymbol{\mu}}_i\delta_{jk})}{(E_k^0 - E_i^0)(E_j^0 - E_i^0)} \mathbf{F}\psi_k^0 - \frac{1}{2}\tilde{\mathbf{F}} \sum_{k \neq i} \frac{\boldsymbol{\mu}_{ik}\tilde{\boldsymbol{\mu}}_{ki}}{(E_k^0 - E_i^0)^2} \mathbf{F}\psi_i^0. \tag{5}$$

In the field the transition moment $\langle\psi_f^0|\boldsymbol{\mu}|\psi_i^0\rangle$ will get contributions from other zero-field transitions, thereby changing from $\boldsymbol{\mu}_{if}$ to $\boldsymbol{\mu}_{if}^{\mathrm{F}}$. The admixture is described by terms linear and quadratic in the field strength. These terms again depend on the orientation of the field.

Now, in order to calculate the electrochromic effect observed as a change in optical density for light of wavenumber $\bar{\nu}_0$ and polarization **e** (**e** is the unit vector in the direction of the electric component of the incident light), one has to proceed as follows: The extinction coefficient of molecules whose transition moments are all oriented parallel to a unit vector **m**, would in the field-free case be

$$\varepsilon_{\mathbf{e},\mathbf{m}}(\bar{\nu}_0) = 3|\tilde{\mathbf{e}} \cdot \mathbf{m}|^2 \varepsilon(\bar{\nu}_0), \tag{6}$$

where $\varepsilon(\bar{\nu}_0)$ is the extinction coefficient of the isotropically oriented molecules at the same wavelength. $\varepsilon(\bar{\nu}_0)$ being proportional to $\bar{\nu}_0|\mu_{if}|^2$, it is more convenient to discuss the quantity

$$\pi_{\mathbf{e},\mathbf{m}} = 3|\tilde{\mathbf{e}} \cdot \mathbf{m}|^2 \frac{\varepsilon(\bar{\nu}_0)}{\bar{\nu}_0} \tag{7}$$

which depends more directly on $|\mu_{if}|$.

According to eqn. (4), in the electric field those transitions will be observed at wavenumber $\bar{\nu}_0$ which in zero field were at wavenumber $(\bar{\nu}_0 - \Delta\bar{\nu}_{if})$.

In that case

$$\pi^{0F}_{\mathbf{e},\mathbf{m}}(\bar{\nu}_0) = 3|\tilde{\mathbf{e}} \cdot \mathbf{m}|^2 \left\{ \frac{\varepsilon(\bar{\nu}_0)}{\bar{\nu}_0} - \frac{\partial \frac{\varepsilon(\bar{\nu}_0)}{\bar{\nu}_0}}{\partial \bar{\nu}_0} \Delta\bar{\nu}_{if} + \frac{1}{2} \cdot \frac{\partial^2 \frac{\varepsilon(\bar{\nu}_0)}{\bar{\nu}_0}}{\partial \bar{\nu}_0^2} (\Delta\bar{\nu}_{if})^2 + \dots \right\} \tag{8}$$

Accounting for the field-induced intensity change (5), one gets:

$$\pi^{F}_{\mathbf{e},\mathbf{m}}(\bar{\nu}) = \pi^{0F}_{\mathbf{e},\mathbf{m}}(\bar{\nu}_0) \frac{|\mu^{F}_{if}|^2}{|\mu_{if}|^2}. \tag{9}$$

At the same time the orientation becomes anisotropic and may, since high rotational quantum states are predominant, be described by Boltzmann statistics. Fixing the orientation of a molecule by the direction cosines γ_ξ of the axes ($\xi = 1,2,3$) of a rectangular molecular co-ordinate system with the field direction, the probability of finding a molecule in an orientation $(\gamma_1,\gamma_2,\gamma_3)$ will be:

$$W(\gamma_1,\gamma_2,\gamma_3)d\tau = \frac{\exp[-\Delta E(\gamma_1,\gamma_2,\gamma_3)/\boldsymbol{k}T]}{\int \exp[-\Delta E/\boldsymbol{k}T]d\tau} d\tau, \tag{10}$$

where $d\tau$ is the element of the solid angle. Averaging $\pi^{F}_{e,m}(\bar{\nu}_0)$ over all orientations requires a rather long calculation. It has been carried through by Liptay.[13] The resulting $\pi^{F}(\bar{\nu}_0)$ may be taken from his paper.

In an actual experiment the relative intensity change of light which passed the sample will be measured rather than $\pi^{F}(\bar{\nu}_0)$ itself. Terms linear in the field vanish and terms of higher power than quadratic are small. One may thus define an electrochromic coefficient

$$L_\chi = \frac{-1}{D|\mathbf{F}|^2 \ln 10} \cdot \frac{I_\chi - I_{\chi,0}}{I_{\chi,0}}, \tag{11}$$

where D is the optical density and I_χ and $I_{\chi,0}$ are the light intensities leaving the sample when the field is on or off, respectively. χ denotes the angle between the field and the electric component of the light, which passes the sample in a direction perpendicular to the field. The theoretical expression for L_χ becomes

$$L_\chi = A + \frac{1}{15hc}\left(\frac{d \ln \varepsilon/\bar{\nu}}{d\bar{\nu}}\right)_{\bar{\nu}_0} B + \frac{1}{30h^2c^2}\left[\left(\frac{d \ln \varepsilon/\bar{\nu}}{d\bar{\nu}}\right)^2_{\bar{\nu}_0} + \left(\frac{d^2 \ln \varepsilon/\bar{\nu}}{d\bar{\nu}^2}\right)_{\bar{\nu}_0}\right] C, \tag{12}$$

with

$$A = \frac{1}{3}\left(\frac{\tilde{\mathbf{R}}^{(1)}}{kT}\,\boldsymbol{\mu}_i + S^{(1)}\right) + \frac{3\cos^2\chi - 1}{30}\left[\frac{3(\tilde{\mathbf{m}}\boldsymbol{\mu}_i)^2 - \boldsymbol{\mu}_i^2}{k^2T^2} + \frac{3}{kT}(\alpha_m - \bar{\alpha}_i) - \frac{(2\tilde{\mathbf{R}}^{(1)} - 3\tilde{\mathbf{R}}^{(2)})\boldsymbol{\mu}_i}{kT} - 2S^{(1)} + 3S^{(2)}\right] \tag{12a}$$

$$B = 5\left(\frac{\tilde{\boldsymbol{\mu}}_i\Delta\boldsymbol{\mu}}{kT} + \frac{3}{2}\Delta\bar{\alpha} + \tilde{\mathbf{R}}^{(1)}\Delta\boldsymbol{\mu}\right) + (3\cos^2\chi - 1) \times \left[\frac{3(\tilde{\mathbf{m}}\boldsymbol{\mu}_i)(\tilde{\mathbf{m}}\Delta\boldsymbol{\mu}) - (\tilde{\boldsymbol{\mu}}_i\Delta\boldsymbol{\mu})}{kT} + \frac{3}{2}(\Delta\alpha_m - \Delta\bar{\alpha}) - \frac{1}{2}(2\tilde{\mathbf{R}}^{(1)} - 3\tilde{\mathbf{R}}^{(2)})\Delta\boldsymbol{\mu}\right] \tag{12b}$$

$$C = 5(\Delta\boldsymbol{\mu})^2 + (3\cos^2\chi - 1)[3(\tilde{\mathbf{m}}\Delta\boldsymbol{\mu})^2 - (\Delta\boldsymbol{\mu})^2]. \tag{12c}$$

In these expressions, $\Delta\boldsymbol{\mu} = \boldsymbol{\mu}_f - \boldsymbol{\mu}_i$ denotes the change in dipole moment, α_m the polarizability in the direction $\mathbf{m}$ of $\boldsymbol{\mu}_{if}$, and $\bar{\alpha}_i = (\alpha_{i11} + \alpha_{i22} + \alpha_{i33})/3$, the mean polarizability in the initial state i. $\Delta\bar{\alpha} = \bar{\alpha}_f - \bar{\alpha}_i$. $\mathbf{R}^{(1)}$ and $\mathbf{R}^{(2)}$ are vectors and $S^{(1)}$ and $S^{(2)}$

scalars formed by sums of products of dipole moments and transition moments of the molecule. They account for the field-induced change of electronic transition moments.

II. MOLECULES IN SOLUTION

In a condensed phase the interaction of a molecule with its surroundings is considerable. Free rotation is quenched, but vibrational and electronic states do not change radically. Accordingly, in solution, rotational transitions in the spectra of free molecules will be replaced by the numerous close-lying transitions between exciton and phonon states. Applying the same type of reasoning as in the last Section, we may again assume a mean field influence on all transitions between two electronic states. The theory outlined above may then tentatively be transferred to solutions.

A difficulty, however, arises as to the internal field $\mathbf{F}$ acting on the molecules. It is different from the external applied field $\mathbf{F}_0$. Usually in non-polar solvents one sets

$$\mathbf{F} = \frac{\varepsilon_{DK} + 2}{3} \mathbf{F}_0, \tag{13}$$

where ε_{DK} is the dielectric constant of the solvent. This is the Lorentz field acting on the molecular dipole of the solute in the special case where the electronic and atomic polarizability of the solute molecule equals the polarizability of the solvent.

In most cases, however, this condition is only approximately fulfilled. Furthermore, in its reaction field $\mathbf{F}_{re}$, the solute molecule is polarized to have an effective dipole moment $\boldsymbol{\mu}' \neq \boldsymbol{\mu}$.

In a careful investigation of such effects Liptay,[13] following Onsager's reasoning,[14] starts by considering a vacancy in the solvent in which a field $\mathbf{F} = f_e \mathbf{F}_0$ is set up by the applied field. The inhomogeneity of this field due to deviations of the shape of the vacancy from an ellipsoid, or due to the molecular structure of the solvent in its neighbourhood, is thus neglected or thought to be averaged out. For a spherical vacancy,[15]

$$f_e = \frac{3\varepsilon_{DK}}{2\varepsilon_{DK} + 1}. \tag{14}$$

A solute molecule inserted into this vacancy stands under the influence of a field

$$\mathbf{F}_{\text{tot}} = \mathbf{F} + \mathbf{F}_{\text{re}}. \tag{15}$$

Again, the reaction field $\mathbf{F}_{\text{re}}$ is thought to be homogeneous and proportional to $\boldsymbol{\mu}'$. For a spherical vacancy of radius a, we have[15]

$$\mathbf{F}_{\text{re}} = f\boldsymbol{\mu}' = a^3 \cdot \frac{2\varepsilon_{DK} - 1}{2\varepsilon_{DK} + 1}\,\boldsymbol{\mu}'. \tag{16}$$

For the initial state, ε_{DK} must be set equal to the low-frequency dielectric constant, whereas for the final state, owing to the relaxation of dipole orientation, ε_{DK} denotes the square of the refractive index. Then

$$\boldsymbol{\mu}' = \boldsymbol{\mu} + \underline{\alpha} f \boldsymbol{\mu}'. \tag{17}$$

(Underlined symbols refer to tensors.)

Proceeding along these lines, Liptay finds that all expressions (12) remain valid if only one sets

$$\mathbf{F} = f_e \mathbf{F}_0 \tag{18}$$

and takes into account that the values of $\boldsymbol{\mu}_i$, $\underline{\alpha}_i$, $\mathbf{R}^{(1)}$, $\mathbf{R}^{(2)}$, $\boldsymbol{\mu}_f$, $\underline{\alpha}_f$, $S^{(1)}$, and $S^{(2)}$ appearing in (12) are related to the corresponding properties of the isolated molecule $\boldsymbol{\mu}_{i0}$, $\underline{\alpha}_{i0}$, $\mathbf{R}_0^{(1)}$, etc., by:

$$\boldsymbol{\mu}_i = (\underline{1} - f\underline{\alpha}_{i0})^{-1}\boldsymbol{\mu}_{i0} \tag{19a}$$

$$\underline{\alpha}_i = (\underline{1} - f\underline{\alpha}_{i0})^{-1}\underline{\alpha}_{i0} \tag{19b}$$

$$\mathbf{R}^{(1)} = (\underline{1} - f\underline{\alpha}_{i0})^{-1}\mathbf{R}_0^{(1)} \tag{19c}$$

$$\mathbf{R}^{(2)} = (\underline{1} - f\underline{\alpha}_{i0})^{-1}\mathbf{R}_0^{(2)} \tag{19d}$$

$$\boldsymbol{\mu}_f = (\underline{1} - f\underline{\alpha}_{f0})^{-1}\boldsymbol{\mu}_{f0} \tag{19e}$$

$$\underline{\alpha}_f = (\underline{1} - f\underline{\alpha}_{f0})^{-1}\underline{\alpha}_{f0} \tag{19f}$$

$$S^{(1)} = (1 - f\bar{\alpha}_{i0})^{-1}S_0^{(1)} \tag{19g}$$

$$S^{(2)} = (1 - f\bar{\alpha}_{i0})^{-1}S_0^{(2)} \tag{19h}$$

Then, in non-polar solvents:

$$\Delta\boldsymbol{\mu} = (\underline{1} - f\underline{\alpha}_{f0})^{-1}\boldsymbol{\mu}_{f0} - (\underline{1} - f\underline{\alpha}_{i0})^{-1}\boldsymbol{\mu}_{i0}, \tag{20a}$$

and

$$\Delta\alpha = (\underline{1} - f\underline{\alpha}_{f0})^{-1}(\underline{1} - f\underline{\alpha}_{i0})^{-1}(\underline{\alpha}_{f0} - \underline{\alpha}_{i0}). \tag{20b}$$

In non-polar solvents $(\underline{1} - f\underline{\alpha}_{i0})^{-1}$, the ratio between the dipole moment of the molecules in the reaction field and the dipole moment of the isolated molecule, ranges between 1·05 and 1·20, whereas the vacancy field is smaller by a factor of 1·08—1·25 than the Lorentz field. Consequently, using the Lorentz field in the evaluation of experimental data yields, in non-polar solvents, a value for the dipole moment that is too small compared with the true dipole moment in solution. However, it approximately equals the dipole moment of the isolated molecule. In view of the uncertainty of f (eqn. 16), which depends strongly on the choice of the form and diameter of the vacancy, we do not think that evaluation of experimental results based on the vacancy field (14), (18), and on the corrections (19) and (20), leads to values of the molecular properties that are more trustworthy. We rather consider the close agreement as a necessary and welcome justification for the naive procedure of using the Lorentz field.

The same situation is met in the determination of dipole moments from dielectric measurements with solutions of polar molecules in non-polar solvents. The molecular dipole moments evaluated according to the Debye or Onsager method usually differ much less from each other than from the dipole moment determined by gas-phase measurements.[15,16] As soon as polar solvents are used, the Lorentz field method will, of course, be unsatisfactory.

The theory outlined above refers to the case of absorption. It may be modified in order to describe also electrically induced polarization and band shifts of fluorescence.[17] If viscous solvents are used, allowance has to be made for the fact that the Langevin distribution of orientation may not be reached during the lifetime of the excited states.[17,18]

III. MEASUREMENT OF ELECTROCHROMISM

From eqns. (11) and (12) one deduces that the order of magnitude of electrochromic effects will be

$$\frac{I_\chi - I_{\chi,0}}{I_{\chi,0}} \approx D\frac{|\boldsymbol{\mu}_i|^2|\mathbf{F}|^2}{k^2T^2}. \tag{21}$$

It is thereby assumed that the dipole orientation effect dominates,

as is usually the case. The optical density D of the solution cannot be chosen to be larger than about 1 or 2 because otherwise stray light might trouble the measurements and the intensity of the light leaving the cell would become too weak. Thus, for a field of 10^5 v/cm, which is the maximum that may be applied to most solvents, and a dipole moment of 1 Debye, we expect at room temperature

$$\frac{I_\chi - I_{\chi,0}}{I_{\chi,0}} \approx 10^{-4}.$$

If a tenth of this should be measured in, say, one second, the flux of quanta entering the phototube must be 10^{10} per sec. It is thus important to use strong light sources and a monochromator of sufficient optical quality, in order not to be forced to use a large spectral bandwidth. A set-up well suited for measurements of electrochromism is shown in Fig. 1.[19]

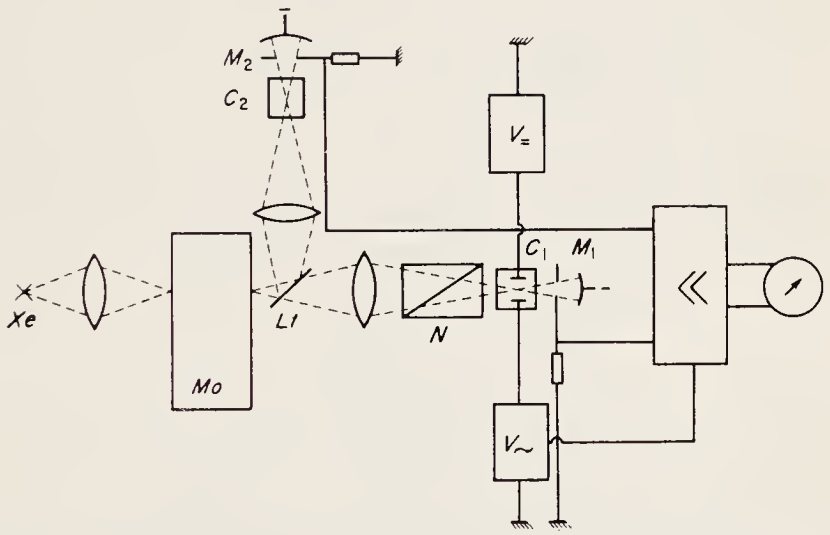


Fig. 1. Apparatus for measurement of the electrochromic effect. C_1 = Sample cell, fitted with electrodes; C_2 = reference cell; Lt = beam splitter (quartz plate); M_1M_2 = photomultipliers; Mo = monochromator; N = polarizer for ultraviolet light; $V_=$ = high-tension d.c. unit; $V\sim$ = high-tension a.c. unit; Xe = xenon lamp; $\ll$ = differential amplifier and phase-sensitive rectifier.

The potential across the cell has the form $V(1 + \cos 2\pi ft)$. The measured effect depends on its square and thus gets a component

of frequency $2f$. This is suppressed by the phase-sensitive rectifier at the exit of the differential amplifier. The frequencies $f = 75$ sec^{-1} (ref. 8) and $f = 125$ sec^{-1} (ref. 20) have been used so far, but probably any other audiofrequency sufficiently different from a harmonic of 50 (or 60 cps) would be equally suitable.

The multiplier M_2 serves as a monitor for variations of the light intensity. If the xenon lamp is driven from a d.c. source without ripple, and if the lamp burns with sufficient stability, M_2 may not be required and an ordinary amplifier may be used instead of the differential one. In choosing the type of the multiplier one has to check whether the amplification of a small alternating signal is independent of the superposition of a relatively bright constant light.

With this experimental set-up, electrostriction, leading to a change of concentration, might give an additional intensity variation. The electrostriction $(\partial V/\partial F)/V$ is related to the pressure-dependence of the dielectric constant by:[21]

$$\frac{1}{V}\left(\frac{\partial V}{\partial F}\right)_{T,P} = -\frac{1}{4\pi}\left(\frac{\partial \varepsilon_{DK}}{\partial P}\right)_{T,F} F$$

in electrostatic units.

Integration, where $(\partial \varepsilon_{DK}/\partial P)_{T,F}$ is assumed to be independent of F, and $(\partial V/\partial F)_{T,P}$ not to depend on P, yields

$$\frac{\Delta V}{V} = \frac{-1}{8\pi}\left(\frac{\partial \varepsilon_{DK}}{\partial P}\right)_{T,F} F^2.$$

$\left(\frac{\partial \varepsilon_{DK}}{\partial P}\right)_{FT}$ is $1{\cdot}5 \times 10^{-10}$ cm^2/dyne for hexane, $1{\cdot}1 \times 10^{-10}$ cm^2/dyne for benzene, and 26×10^{-10} cm^2/dyne for ethanol.[22] The relative contraction in a field of 10^5 volt/cm is thus $-6{\cdot}6 \times 10^{-7}$, $-4{\cdot}8 \times 10^{-7}$ and $-1{\cdot}14 \times 10^{-5}$, respectively, and leads to a relative intensity change $\Delta I/I_0$ of $-1{\cdot}5 \times 10^{-6}$, $-1{\cdot}1 \times 10^{-6}$, and $-2{\cdot}6 \times 10^{-5}$, respectively, for these three solvents (with $D = 1$). In hexane and benzene it is thus well below the measuring sensitivity reached to date.

Another effect might arise from the change in internal pressure. The volume contractions just estimated correspond to pressure

increases of $\Delta P = 0{\cdot}005$, $0{\cdot}007$, and $0{\cdot}12$ atm in benzene, hexane, and ethanol, respectively. The order of magnitude of spectral shifts with pressure was found to be 10^{-2} Å/atm.[23]

With

$$\frac{\Delta I}{I_0} = -2{\cdot}3\frac{\Delta\varepsilon}{\varepsilon}D = 2{\cdot}3^2\left(\frac{\mathrm{d}\log\varepsilon}{\mathrm{d}\lambda}\right)\left(\frac{\mathrm{d}\lambda}{\mathrm{d}P}\right)\Delta PD.$$

At optical density 1, with $\Delta P = 10^{-2}$ atm and 2×10^{-12} Å^{-1} as a representative value for $\mathrm{d}\log\varepsilon/\mathrm{d}\lambda$ from measured solution spectra, we find

$$\left(\frac{\Delta I}{I_0}\right)_{\text{pressure}} \approx 10^{-5}.$$

The spectral shift due to electrostrictive increase of internal pressure thus might affect the results in unfavourable cases (small dipole moment, sharp bands).

Measurements of pressure-dependence of band contours have hitherto not been carried out with the aim of correcting electrochromic effects. We have just started investigations of this kind.

Electrostrictive effects may be eliminated by using an experimental arrangement shown in Fig. 2.[8,19] Less information is,

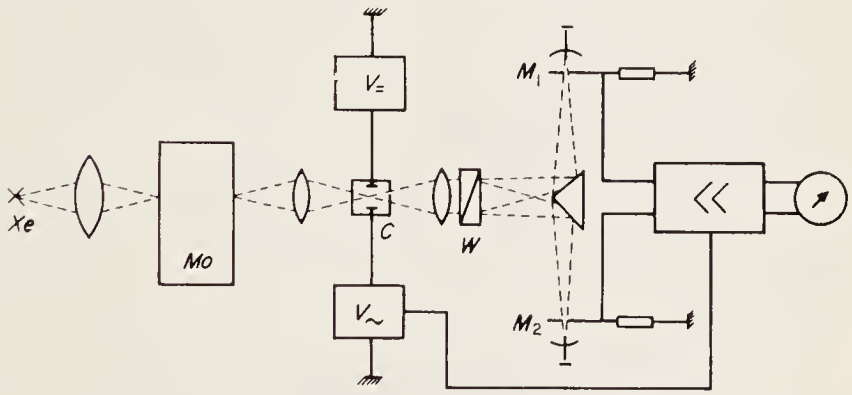


Fig. 2. Alternative apparatus for measurement of the electrochromic effect.

C = Sample cell; M_1M_2 = photomultipliers; Mo = monochromator; $V_=$ = high-tension d.c. unit; $V\sim$ = high-tension a.c. unit; W = Wollaston plate for ultraviolet light; Xe = xenon lamp; $\ll$ = differential amplifier and phase-sensitive rectifier.

however, obtained than with the set-up of Fig. 1 since the intensity changes corresponding to terms in eqns. (12) not depending on χ cancel.

In order to determine A, B, and C of equation (12) measurements at different wavelengths have to be taken. The coefficients of $(3\cos^2\chi - 1)$ in eqns. (12a), (12b), and (12c) can be identified by measuring the effect for at least two different angles of polarization χ of the electric vector of the light beam with respect to the electric field. A further separation of these expressions might be achieved by varying the temperature. However, the range of possible temperatures is relatively small, and the accuracy of measurement is not sufficient to draw advantage from small temperature variations. A very high temperature, however, may be simulated by embedding the molecules in a rigid matrix in which no orientation occurs. The matrix may be an organic glass (e.g. EPA). Investigations of this type are being carried through but are not yet complete. Powers, Kumamoto, and Heller[24,25] observed bandshifts in polystyrene matrices.

In the general case of a molecule without symmetry, eqns. (12) do not allow determination of all the unknowns contained therein from measurements of electrochromism alone. A plane of symmetry already is of great help. For instance, with C_{2v} symmetry the direction of the dipole moments of the ground and the excited state is known and only two directions are possible for π–π^* transition moments. If a molecule has a centre of symmetry, the dipole moment vanishes, but orientation may take place through the anisotropy of the polarizability.[9]

The molecular properties to be taken from such measurements are the absolute orientation of transition moments, as well as the change in dipole moment ($\Delta\mu$) and the change in polarizability $\Delta\alpha$ upon excitation.

IV. APPLICATIONS

A. Polarization of Electronic Transitions

Investigation of electrochromism was initiated by W. Kuhn, Dührkop, and Martin[7] in 1939 in order to prove that optical transitions were anisotropic. Later, as different quantum-mechanical approximations for calculating electronic transitions

became available, the problem of assignment of theoretical transitions to observed bands arose.[8] It was felt that, the polarization as well as the wavelength and the intensity, of a transition with respect to the molecular framework would be a most valuable criterion for making assignments. Many methods such as fluorescence polarization,[26] dichroism of stretched polymer films containing the molecule of interest as a solute,[27] and photodichroism[28] yield only the relative orientation of different transition moments. Observation of crystalline dichroism is often complicated by strong molecular interactions and the detailed crystal structure is a prerequisite. Electrochromism, however, allows determination of the direction of a transition moment provided the molecule has a dipole moment larger than two Debye units or an anisotropy of polarizability of known sign.

Dichroism induced by an electric field was initially observed[29] for solutions of a number of anthraquinone derivatives of symmetry C_{2v}. If the polarizations of transitions in the unsubstituted anthraquinone are sought, these may be extrapolated from its halogen derivatives. The halogen substituents have little effect on the electronic absorption spectrum but nevertheless lead to a large enough dipole moment. Comparison of the results with Kuboyama's[30] Hückel calculations permits the assignment of the experimental 4·85 ev transition to a calculated one. Another transition, predicted to appear at longer wavelength, must, because of its polarization, be assigned to some experimental transition at shorter wavelength. This again shows that not even the sequence of the transitions of round field molecules (Platt[31]) may be correctly obtained by simple Hückel calculations.

Investigations of tropone, benzotropone, and naphthotropone[32] revealed the longest-wavelength absorption maximum as due to superposition of two perpendicularly polarized transitions. Hückel calculations with a single empirical value of the Coulomb integral for oxygen for all three compounds yielded results in good agreement with observed wavelength, intensity, and polarization. Pople–Pariser–Parr calculations have been carried out for a number of monosubstituted and *para*-disubstituted benzenes,[33] and the results have been compared with experimental values with respect to wavelength, intensity, and polarization of the transitions, as well as with respect to excited-state π-dipole

moments. For each compound the assignment seemed unambiguous. The absolute polarizations of transitions of a number of other molecules have also been determined by means of electrochromism, amongst others benzonitrile, *o*-phthalonitrile, *m*-phthalonitrile, 2,7-naphthalenedinitrile, 9-anthracenenitrile,[34] and some 4,4′-disubstituted biphenyls and stilbenes.[35]

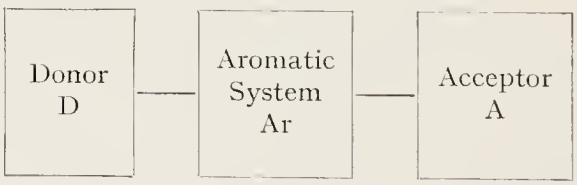
Absolute transition-moment directions of 5-nitro-1,3-phenylenediamine, 3,5-dinitroaniline, 3,6-dinitrocarbazole, and carbazole may be obtained from a recent thesis by Eberlein.[20]

In the measurement of the electrochromic effect, greater sensitivity would sometimes be desirable. The accuracy achievable for the relative orientation of transition moments such as fluorescence polarization or dichroism of stretched film seems to be rather better. It would thus be a good combination to determine the absolute orientation of one transition from electrochromism and to investigate the polarization of the others by some different method.

B. Determination of Dipole Moments in Exited States

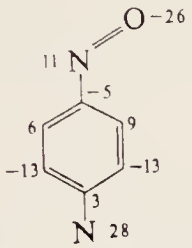
This application of electrochromism has been reviewed elsewhere in two places.[36,37] The values available so far are compiled in the annexed tables. Where possible, values taken from methods other than electrochromism are included for comparison. The accuracy of the excited-state dipole moments is about 10 per cent.

The structure of a number of compounds listed in the table corresponds to the following scheme:

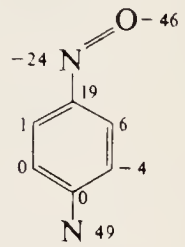


It is seen that the dipole moments in the excited states are larger than in the ground state. In terms of valence-bond theory this may be interpreted as an increased contribution of the mesomeric forms $D^+=Ar=A^-$ and $D—Ar^+=A^-$. From the absolute value of excited-state dipole moments it follows, however, that none of these forms plays the major role. Their relative contributions have been estimated by Grinter and Heilbronner,[42] using the

method of molecules in molecules.[43] Choosing parameters, which may be appropriate for a molecule such as *N*,*N*-dimethyl-*p*-nitrosoaniline, Grinter and Heilbronner found that an increase of 19 per cent of the mesomeric form D—Ar^+=A^- is responsible for the increase in dipole moment upon excitation to the lowest excited singlet π–π^* state, the form D^+=Ar=A^- not contributing at all. The corresponding increase in dipole moment is about 2 D, which is to be compared with the experimental value of 7 D. SCF–PPP calculations on the same molecule[33] yield the following charge distributions (in hundredths of the charge of a proton):



Ground state



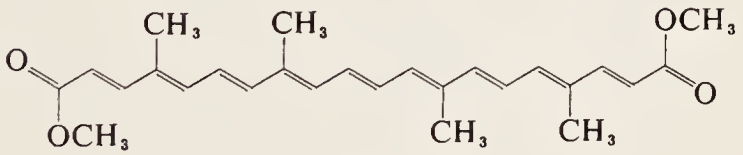
First excited π–π^* singlet

The change in dipole moment of 70·1 D connected with this charge reorganization is somewhat larger than found experimentally.

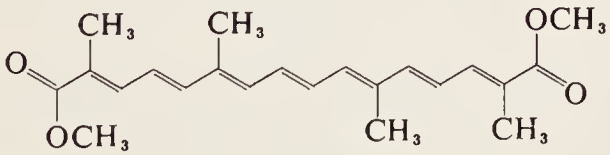
This and some further examples from the table may illustrate the degree of agreement reached so far between experiment and semiempirical calculations.

C. Polarizability in Excited States

The anisotropy of polarizability in the ground state in molecules having a non-vanishing dipole moment generally contributes little to the orientation in an electric field. Similarly if there is a change



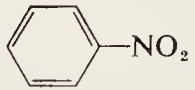
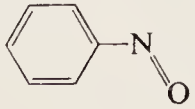
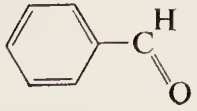
(I)

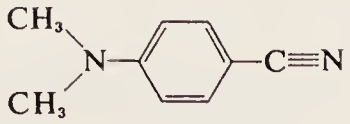
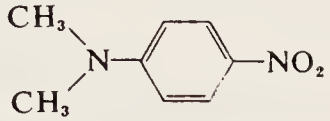
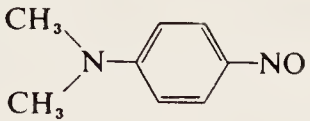
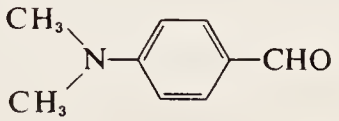


(II)

Dipole moments of excited molecular states (in Debye units)

Solvent: H = hexane, B = benzene, D = dioxane.
States: G = ground state, S_i = i-th excited singlet state.

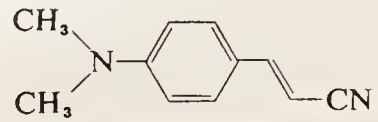
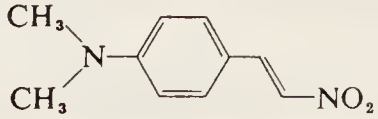
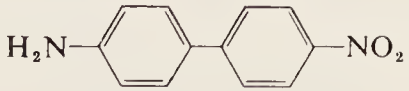
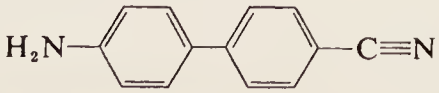
Molecule	Solvent	State	Method of determination					
			Dielectric measurement	Solvent shift: Evaluation by Lippert[39]	Solvent shift: Evaluation by Bilot and Kawski[40]	Effect of electric field on absorption	Effect of electric field on fluorescence	Calc. π-dipole moment
	H	G S_1 S_2 S_3	4·2			 9 ± 2[33]		5·5 8·7 12·4[33]
	H	G S_1^* S_2 S_3	3·14			12·2[33]		2·42 8·3 9·8 7·4[33]
	H	G S_1 S_2 S_3	2·75			 7·1 6·3[33]		2·78 2·6 4·3[33]

	D	G S_1	6·6	23		12·5[34]	11·1– 14·9[38]	
	H	G S_1 S_2 S_3	6·85			— 14·3 11·8[33]		8·8 14·0 20·7 15·4
	H	G S_1* S_2 S_3	6·45			13·5 — 13·4[33]		5·96 16·1 9·7 14·9[33]
	H	G S_1 S_2 S_3	5·6			13·3[33] —		4·58 8·3 11·3 10·2[33]

* The long-wavelength n–π^* transition has not been included.

Dipole moments of excited molecular states (in Debye units) (*continued*)

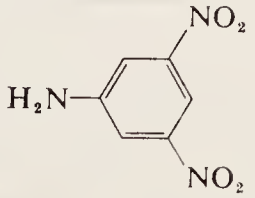
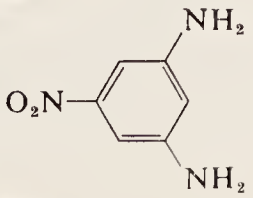
Solvent: H = hexane, B = benzene, D = dioxane.
States: G = ground state, S_i = i-th excited singlet state.

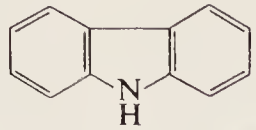
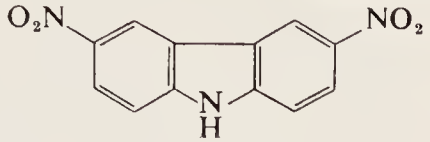
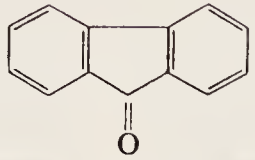
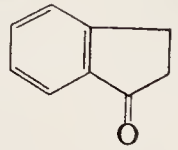
Molecule	Solvent	State	Method of determination					
			Dielectric measurement	Solvent shift: Evaluation by Lippert[39]	Solvent shift: Evaluation by Bilot and Kawski[40]	Effect of electric field on absorption	Effect of electric field on fluorescence	Calc. π-dipole moment
	H	G	6·95					
		S_1		14[41]		14[34]		
	B	G	7·7					
		S_1		18		18[34]	17·9[38]	
	B	G	6·0					
		S_1		18	15·5	23[34]	22·4[38]	
	B	G	6·0					
		S_1				16·5[34]	15·3–13·0[38]	

	B	G	5·8					
		S_1		25	23·5	23^{34}	$19{\cdot}2–18{\cdot}6^{38}$	
	B	G	6·5					
		S_1				22^{34}	$23{\cdot}4^{38}$	
	B	G	7·1					
		S		32	25	$26{\cdot}5^{34}$	$25{\cdot}1^{38}$	
	D	G	7·1					
		S_1		29		20^{34}	$21{\cdot}2$ $20{\cdot}2^{38}$	

Dipole moments of excited molecular states (in Debye units) (*continued*)

Solvent: H = hexane, B = benzene, D = dioxane.
States: G = ground state, S_i = i-th excited singlet state.

Molecule	Solvent	State	Method of determination					
			Dielectric measurement	Solvent shift: Evaluation by Lippert[39]	Solvent shift: Evaluation by Bilot and Kawski[40]	Effect of electric field on absorption	Effect of electric field on fluorescence	Calc. π-dipole moment
 20)	D	G S_1	6·22			5·9 11·9		
 20)	D	G S_1 S_2	5·98			5·35 12·4 16·7		

	20)	D	G S_1 S_2	2·21			1·91 3·1 3·5		
	20)	D	G S_1				6·65 13·9		
	20)	D	G S_1^*	3·37			4·8		
	20)	D	G S_1^*	3·55			3·2 4·4		

* The weak long-wavelength transition has not been included.

in dipole moment the change in polarizability upon excitation is of minor influence on the bandshift. However, electrochromic effects have been observed[9] with non-polar molecules of highly anisotropic polarizability such as bixin dimethyl ester (I) and crocetin dimethyl ester (II). The presence of only a weak *cis*-peak in the ultraviolet spectrum[44] makes the all-*trans*-configuration of these molecules highly probable. Further, the sign of the dichroism in the electric field shows that the molecules are oriented parallel to the field direction. If, owing to some *cis*-contribution, the molecules had an angular form, the resulting dipole moment would be approximately perpendicular to the transition moment of the longest-wavelength absorption, and dichroism of opposite sign should result.

From the measurements of electrochromism the magnitude of the anisotropy of polarizability of molecule (I) was found to be:[19]

$$\alpha_{xx} - \bar{\alpha} = 90 \times 10^{-24}\ \mathrm{cm}^3,$$

whereas the change in the longitudinal polarizability upon excitation was:

$$\Delta\alpha_{xx} = 930 \times 10^{-24}\ \mathrm{cm}^3.$$

The latter value has been estimated on the assumption that $\Delta\alpha_{yy} = \Delta\alpha_{zz} = 0$.

Similarly for molecule (II), $\Delta\alpha_{xx} = 460 \times 10^{-24}\ \mathrm{cm}^3$, was obtained.

Rough calculation of $\Delta\alpha_{xx}$ on the basis of the free-electron theory[9] showed that it depends strongly on the difference of single- and double-bond lengths. If equal bond lengths are assumed, $\Delta\alpha_{xx}$ almost vanishes, whereas with a difference in bond length observed for polyenes[45,46] or taken from theoretical calculations[47,48] it has the right order of magnitude.

V. SUMMARY

This review of electrochromism describes the present state of theory and experiment, as well as the results and applications. It is also shown under what approximations a connection may be established between measured changes in the optical density of solutions induced by an external electric field and the properties of relatively large solute molecules. The molecular

properties that may be determined are the absolute direction of transition moments and dipole moments and polarizabilities of excited states. In particular, little use has been made to date of the last-mentioned possibility.

The author thanks Dr. Wagnière for valuable criticism and comments.

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THE EVALUATION OF MOLECULAR INTEGRALS FOR SLATER-TYPE ORBITALS

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I. INTRODUCTION

One of the early steps toward the construction of a tractable theory of the electronic structure of atoms and molecules was the introduction by Slater (1930) of atomic orbitals with a radial dependence of the form $r^n \exp(-\delta r)$. These, now universally known as Slater-type orbitals, have proved to be invaluable in discussions of both atoms and molecules. Slater-type orbitals possess the virtue of having correct limiting behavior at both small and large r, and they appear to provide a highly efficient description of the electron distribution in many electronic systems. However, in calculations for diatomic and, particularly, polyatomic molecules, the use of Slater-type orbitals leads to integrals which are notoriously difficult to evaluate, and some investigators have considered the use of other, less inherently desirable orbitals as an alternative to the integral evaluations.* The advent of high-speed computational equipment has provided new channels for attack on the integral problem, and it now appears practical to handle integrals involving Slater-type orbitals in arbitrary geometrical configurations. In this article, we describe the methods that we have found to be useful in evaluating all the integrals needed to make energy calculations for polyatomic molecules. Our methods apply to orbitals of any quantum number, and have currently been implemented for $n \leqslant 7$, $l \leqslant 3$, $|m| \leqslant l$. In addition, the orbitals may be situated at completely arbitrary spatial points, and each orbital may have its own completely arbitrary axial orientation.

The many investigators who have examined the integral evaluation problem have employed a great variety of techniques. To begin, it is found that one-center integrals are easily evaluated by using spherical harmonic expansions about the single center. For two-center integrals, several procedures have proved to be useful. One method for studying two-center integrals involves expansion of the orbitals on one center about the other center, as first suggested by Coolidge (1932), further developed by Landshoff (1936),

* The most fruitful alternative suggestion has been the use of Gaussian orbitals, on which the pioneering work was done by Boys (1950, 1960). For further work on Gaussians, see, among others, Browne and Poshusta (1962), Harris (1963), and Krauss (1963).

Löwdin (1947), and Barnett and Coulson (1951). A second possibility is the use of ellipsoidal coordinates with the two orbital centers as foci. A full bibliography of this method is given by Kotani and his collaborators (1955), and a more recent description has been given by one of the present authors (Harris, 1960). It should be noted that the ellipsoidal expansion is not the only reasonable two-center expansion; it is also possible to use a bipolar spherical expansion as discussed, for example, by Carlson and Rushbrooke (1950), and by Buehler and Hirschfelder (1951). An elegant discussion of some properties of bipolar expansions has been given by Nozawa (1954, 1965), who also suggested their use for integral evaluation; and Ellis and Ros (1966) recently proposed an integral evaluation method of this type.

Three- and four-center integrals may be expanded about a single center, as suggested by various workers and illustrated in detail in the present communication. It is also practical to evaluate some of these integrals by ellipsoidal expansion methods. Alternatives to these expansion methods have been extensively considered, and include the use of extensive numerical integrations, either by conventional quadrature methods (cf. Barnett, 1963; Magnusson and Zauli, 1961) or by Monte Carlo procedures (Conroy, 1964). Further possibilities include the use of integral transformations to produce more easily integrable forms (Shavitt and Karplus, 1962, 1965; Shavitt, 1963; Bonham, Peacher, and Cox, 1964). If an integral transformation method is used, there remains the problem of inverting the transform after the spatial integrations have been carried out. This normally results in additional integrations which, hopefully, will be of simpler forms than those which the method has avoided.

An additional technique which has proved to be useful in conjunction with the expansion methods for multi-center integrals is the application of transform convolution theorems. As observed by Prosser and Blanchard (1962), certain integrals may be regarded as convolutions and may therefore be rewritten in terms of the Fourier transforms of the quantities appearing in the integrand. Geller (1962, 1964) has shown that this device is particularly useful in the evaluation of two-center integrals of the Coulomb type.

The particular evaluation method to be chosen for each integral depends upon a number of interrelated factors. From a practical

point of view, the prime consideration is the minimization of computational effort in obtaining results at the desired level of accuracy. A secondary, but far from negligible, requirement is that the methods be sufficiently general for each integral not to be a special case in itself. Otherwise, the amount of programming which may be required becomes excessive and it may be nearly impossible to determine whether the computational methods are error-free. We have found that a particularly effective means of increasing computational efficiency is to arrange the work so that much of the intermediate material generated for one integral can also be used for other related integrals. Our methods for electron-repulsion integrals utilize this principle; we generate arrays of data for each charge distribution and re-use the arrays for every integral in which the charge distribution occurs.

One of the most significant factors influencing computational speed appears to be the rate of convergence of the series expansions that are employed. Convergence is optimized by choosing a method in which the singular points of the orbitals are made to coincide with the singular points of the coordinate system in which the expansion is made. Hence, two-center integrals converge best in ellipsoidal coordinates. It is found that it is far more important to place the orbital centers at the singular coordinate points than so to place a nucleus of attraction. Accordingly, two-center nuclear attraction integrals in which both orbitals are on one center (with the nucleus on the other center) converge well in a spherical expansion about the orbital center, while three-center nuclear attraction integrals converge slowly in spherical expansions, but very rapidly in an ellipsoidal expansion when the orbital centers are used as foci.

The main part of our exposition is organized as follows. We start with a survey of the notations and definitions to be employed in the work. There next follows a detailed discussion of the rotational coordinate transformations needed to relate quantities originally described in coordinate systems with arbitrary relative orientations. We then proceed to a discussion of specific integrals: first, we describe the one-electron, two-center integrals which are best treated in ellipsoidal coordinates; and we then discuss, also in ellipsoidal coordinates, the three-center nuclear attraction integrals. The evaluation of one-center electron repulsion integrals

by a spherical harmonic expansion method is next described. Then we turn to the two-center Coulomb-type electron repulsion integrals, treated by a Fourier convolution method, which effectively reduces them to a one-center problem. Ellipsoidal methods for general two-center electron repulsion integrals are next reviewed. Finally, we discuss a one-center expansion method for general multi-center electron repulsion integrals. Computation times and accuracy, and some typical results, are cited in the closing section of the main text. The appendices contain details of some of the manipulations, and properties of some of the special functions required in the work. There is little new material in the appendices, but it is convenient to have all the necessary formulae collected in one source and in a consistent notation.

The methods we describe have all been tested, both as to efficiency and accuracy of computation. In the checking of our formulations and numerical values, considerable assistance was provided by the landmark papers of Roothaan (1951) and Rüdenberg (1951), by the tables and formulas of Kotani and his collaborators (1955), of Preuss (1956), and of Miller, Gerhäuser, and Matsen (1959), and by the computer programs of Pitzer, Wright, and Barnett (1963).

II. GENERAL CONSIDERATIONS

A. Orbitals and Integrals

We shall be concerned with Slater-type orbitals centered at various points in space. Let Ψ_a stand for an orbital centered at the point **A**, where **A** is described by the spherical polar coordinates (R_a, Θ_a, Φ_a) relative to a fixed axial frame centered at a point **P**. This axial frame will be the same for all orbitals under consideration. Notice that we use capital letters to refer to the coordinates of orbital centers; we shall use capitals also to refer to nuclear positions, and shall invariably use lower case letters for electronic coordinates. In terms of a spherical polar coordinate system (r_a, θ_a, ϕ_a) centered at **A**, the functional form of Ψ_a is taken to be:

$$\Psi_a = r_a^{n_a-1} \exp(-\delta_a r_a) P_{l_a}^{m_a}(\cos\theta_a) \cos(m_a\phi_a), \qquad m_a \geqslant 0 \quad (1a)$$

$$\Psi_a = r_a^{n_a-1} \exp(-\delta_a r_a) P_{l_a}^{m_a}(\cos\theta_a) \sin(|m_a|\phi_a), \qquad m_a < 0 \quad (1b)$$

Here n_a, l_a, and m_a are quantum numbers characterizing Ψ_a, and δ_a is a parameter controlling the scale of Ψ_a. The associated Legendre functions P_l^m appearing in eqs. (1) are as defined in Appendix B. Note that our conventions regarding coordinate systems are such that for orbital centers or nuclei, the subscripts, as in (R_a, Θ_a, Φ_a), refer to the location of the center or nucleus, in this case **A**, relative to a fixed coordinate frame, while subscripts to electronic coordinates, as in (r_a, θ_a, ϕ_a), refer to the center which is the origin of the coordinate system then in use.

As we do not wish to restrict the orientation of the axial system from which (r_a, θ_a, ϕ_a) is measured, we assume that this axial system has an orientation which may be reached from that of the fixed axial frame centered at **P** by rotation through Eulerian angles $(\alpha_a, \beta_a, \gamma_a)$. We shall use the definitions of Eulerian angles and related quantities as given in Appendix A. We thus see that the orbital Ψ_a is at a position and orientation specified by the six quantities R_a, Θ_a, Φ_a, α_a, β_a, γ_a, while the functional form of Ψ_a is determined by the quantum numbers n_a, l_a, m_a, and by the screening parameter δ_a. Notice that we have chosen to use real, rather than complex, orbitals, and that Ψ_a is unnormalized. We define additional orbitals Ψ_b, Ψ_c, Ψ_d in a manner analogous to that used for Ψ_a.

The one-electron integrals to be discussed include the *overlap integral*:

$$S_{ab} = \int \Psi_a^*(\mathbf{r}) \Psi_b(\mathbf{r})\, d\mathbf{r}, \tag{2}$$

the *kinetic energy integral*:

$$T_{ab} = -\tfrac{1}{2} \int \Psi_a^*(\mathbf{r}) \nabla^2 \Psi_b(\mathbf{r})\, d\mathbf{r}, \tag{3}$$

and the *nuclear attraction integral*:

$$V_{ab,c} = \int \Psi_a^*(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{C}|} \Psi_b(\mathbf{r})\, d\mathbf{r}, \tag{4}$$

where **C** is the location of a nucleus. It is to be understood that **r** and **C** are in the same coordinate system, that the integrations extend over all three-dimensional space, and that $\Psi_a^*(\mathbf{r})$ and $\Psi_b(\mathbf{r})$ stand for the expressions resulting when these quantities, defined as in eq. (1a) or (1b), are transformed into the coordinate

system used for **r** and **C**. The two-electron integrals under discussion are the *electron repulsion integrals*:

$$X_{ab,cd} = \int \Psi_a^*(\mathbf{r}_1)\Psi_b(\mathbf{r}_1)\,\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\,\Psi_c^*(\mathbf{r}_2)\Psi_d(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2, \qquad (5)$$

where $\mathbf{r}_i$ refers to the coordinates of the i-th electron, with $\mathbf{r}_1$ and $\mathbf{r}_2$ in the same coordinate system. The orbital product for one electron, *i.e.* $\Psi_a^*\Psi_b$ or $\Psi_c^*\Psi_d$, is referred to as a *charge distribution*, and may be a *one-center* or a *two-center* charge distribution depending upon whether or not centers A and B, or C and D, coincide. An electron repulsion integral, whose charge distributions are both one-center, but at different centers, is referred to as being of *Coulomb type*.

B. Rotational Coordinate Transformations

In this work, the main problem associated with rotational coordinate transformations is the effect of the transformation upon spherical harmonic functions. Letting (θ, ϕ) be angular coordinates in some axial system and (θ', ϕ') be the corresponding coordinates in an axial system obtained from the first by a rotation described by Eulerian angles (α, β, γ), we have

$$P_l^m(\cos\theta)e^{im\phi} = \sum_{\sigma=-l}^{l} D_l^{m,\sigma}(\alpha, \beta, \gamma)P_l^\sigma(\cos\theta')e^{i\sigma\phi'} \qquad (6)$$

with (see, for example, Edmonds, 1957)

$$D_l^{m,\sigma}(\alpha, \beta, \gamma) = e^{im\alpha + i\sigma\gamma}\mathrm{d}^l(\cos\beta)_{m,\sigma}, \qquad (7)$$

$$\mathrm{d}^l(t)_{m,\sigma} = \frac{(l+m)!}{(l+\sigma)!}\left(\frac{1+t}{2}\right)^l \sum_s (-1)^{s+m}\binom{l-\sigma}{m+s} \times \binom{l+\sigma}{l-s}\left(\frac{1-t}{1+t}\right)^{s+(m+\sigma)/2}, \qquad m, \sigma \geqslant 0 \qquad (8)$$

$$\mathrm{d}^l(t)_{m,\sigma} = \mathrm{d}^l(t)_{-m,-\sigma} = (-1)^{l+m+\sigma}\,\mathrm{d}^l(-t)_{m,-\sigma} = (-1)^{l+m+\sigma}\,\mathrm{d}^l(-t)_{-m,\sigma} \qquad (9)$$

The sum over s in eq. (8) includes all values for which the binomial coefficients are defined. The most efficient way to generate the

coefficients $d^l(t)_{m,\sigma}$ is not by direct use of eq. (8), but by recurrence methods such as those outlined in Appendix A. We note that, according to eq. (6), rotation of the coordinate system transforms a spherical harmonic into a linear combination of spherical harmonics of the same l value, but with a range of m values.

Frequently we shall deal with a rotational transformation defined, not directly by rotations (α, β, γ), but instead implicitly in terms of an initial axial orientation $(\alpha_1, \beta_1, \gamma_1)$ and a final orientation $(\alpha_2, \beta_2, \gamma_2)$, both sets of Eulerian angles referring to orientations relative to a common reference frame. The angles (α, β, γ) can be specified in terms of $(\alpha_1, \beta_1, \gamma_1)$ and $(\alpha_2, \beta_2, \gamma_2)$, according to the detailed formulae given in Appendix A. We can indicate the relationship between these three sets of angles by the symbolic equation

$$(\alpha, \beta, \gamma)(\alpha_1, \beta_1, \gamma_1) = (\alpha_2, \beta_2, \gamma_2). \tag{10}$$

The formulae of Appendix A, and the computer program implementing them, can then be thought of as a procedure for solving equations of the form given in eq. (10) for the quantity (α, β, γ).

The ideas set forth in the preceding paragraph may be applied to another problem of frequent occurrence in the present work, namely, the determination of the angular coordinates (θ', ϕ') in a rotated frame of the ray designated in the unrotated frame by (θ, ϕ), the rotation being assumed to be described by Eulerian angles (α, β, γ). The rotation carrying the polar axis from its reference position to the ray defined by (θ, ϕ) has Eulerian angles (ϕ, θ, x), where x is arbitrary. Similarly, the rotation to the ray defined by (θ', ϕ') has Eulerian angles (ϕ', θ', x'), where, again, x' is arbitrary. We therefore see that the ray described before rotation by (θ, ϕ) may alternatively be described in terms of an axial rotation (α, β, γ) followed by excursion to the direction (θ', ϕ'), or, symbolically,

$$(\phi', \theta', x')(\alpha, \beta, \gamma) = (\phi, \theta, x). \tag{11}$$

Solution of eq. (11) for any arbitrary x, say $x = 0$, yields θ' and ϕ'.

Another problem that we shall encounter is the description of the single rotation equivalent to the successive application of two given rotations. Looking at eq. (10), we see that $(\alpha_2, \beta_2, \gamma_2)$ can

be regarded as the result of applying $(\alpha_1, \beta_1, \gamma_1)$, followed by (α, β, γ). If now $(\alpha_2, \beta_2, \gamma_2)$ is unknown, we may solve for it by multiplying left- and right-hand sides of eq. (10) by $(\alpha_1, \beta_1, \gamma_1)^{-1}$, getting

$$(\alpha_2, \beta_2, \gamma_2)(\alpha_1, \beta_1, \gamma_1)^{-1} = (\alpha, \beta, \gamma). \tag{12}$$

This equation is now in the correct form for applying our formulae to obtain $(\alpha_2, \beta_2, \gamma_2)$, provided we make use of the fact that

$$(\alpha_1, \beta_1, \gamma_1)^{-1} = (\pi - \gamma_1, \beta_1, \pi - \alpha_1). \tag{13}$$

We conclude this section by rewriting eqs. (10)–(12) in forms more directly useful for computation. Letting ROT $(\alpha_1, \beta_1, \gamma_1, \alpha_2, \beta_2, \gamma_2, \alpha, \beta, \gamma)$ stand for a computational procedure whereby the rotation from orientation $(\alpha_1, \beta_1, \gamma_1)$ to $(\alpha_2, \beta_2, \gamma_2)$ is computed and stored as (α, β, γ), we obviously generate the transformation from $(\alpha_1, \beta_1, \gamma_1)$ to $(\alpha_2, \beta_2, \gamma_2)$ by calling ROT $(\alpha_1, \beta_1, \gamma_1, \alpha_2, \beta_2, \gamma_2, \alpha, \beta, \gamma)$. This is the equivalent of the direct use of eq. (10). To find the angular coordinates (θ', ϕ') corresponding to (θ, ϕ) after an axial transformation (α, β, γ), we call, corresponding to eq. (11), ROT $(\alpha, \beta, \gamma, \phi, \theta, 0, \phi', \theta', x')$. Finally, to find the transformation corresponding to $(\alpha_1, \beta_1, \gamma_1)$ followed by $(\alpha_2, \beta_2, \gamma_2)$, we call ROT $(\pi - \gamma_1, \beta_1, \pi - \alpha_1, \alpha_2, \beta_2, \gamma_2, \alpha, \beta, \gamma)$, obtaining the result as (α, β, γ).

C. Expansion Formulae

We shall make repeated use of Green's function expansions in both spherical and ellipsoidal coordinates. In spherical coordinates the expansion assumes the form (see, for example, Morse and Feshbach, 1953, p. 1274):

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{(l - |m|)!}{(l + |m|)!} \frac{r_-^l}{r_+^{l+1}} P_l^m(\cos\theta_1) P_l^m(\cos\theta_2) e^{im(\phi_2 - \phi_1)}, \tag{14}$$

where $\mathbf{r}_1$ is the point (r_1, θ_1, ϕ_1), $\mathbf{r}_2$ is (r_2, θ_2, ϕ_2), and r_+ and r_- refer to the greater and lesser, respectively, of r_1 and r_2.

We define an ellipsoidal coordinate system (ξ, η, ϕ) based on foci at **A** and **B** by the relations $\xi = (r_a + r_b)/R$, $\eta = (r_a - r_b)/R$, with r_a and r_b representing the distances from the coordinate point

to **A** and **B**, respectively, and R denoting $|\mathbf{A} - \mathbf{B}|$. The azimuthal angle ϕ is measured from a reference half-plane bounded by the line through **A** and **B**. In this coordinate system, the expansion corresponding to eq. (14) is (Neumann, 1878):

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{2}{R} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-1)^m (2l+1) \left[\frac{(l-|m|)!}{(l+|m|)!}\right]^2 \times P_l^m(\xi_-) Q_l^m(\xi_+) P_l^m(\eta_1) P_l^m(\eta_2) e^{im(\phi_2 - \phi_1)}, \quad (15)$$

where $\mathbf{r}_1$ is (ξ_1, η_1, ϕ_1), $\mathbf{r}_2$ is (ξ_2, η_2, ϕ_1), and ξ_+ and ξ_- refer to the greater and lesser, respectively, of ξ_1 and ξ_2. In eq. (15), the Legendre functions P_l^m and Q_l^m are as defined in Appendix B. Note that the definitions depend upon the range of the argument, which, for η, is $-1 \leqslant \eta \leqslant +1$, and for ξ, $\xi \geqslant 1$.

We shall also make use of the spherical wave expansion for $\exp(\pm i\mathbf{k} \cdot \mathbf{r})$, where, in spherical cooordinates, $\mathbf{r}$ is (r, θ, ϕ) and $\mathbf{k}$ is $(k, \bar{\theta}, \bar{\phi})$. This expansion is (see, for example, Morse and Feshbach, 1953, p. 1466):

$$\exp(\pm i\mathbf{k} \cdot \mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (\pm i)^l (2l+1) \frac{(l-|m|)!}{(l+|m|)!} \times j_l(kr) P_l^m(\cos\theta) P_l^m(\cos\bar{\theta}) e^{im(\phi - \bar{\phi})}. \quad (16)$$

Here $j_l(kr)$ is a spherical Bessel function as defined in Appendix C.

III. ONE-ELECTRON, TWO-CENTER INTEGRALS

A. Transformation into Ellipsoidal Integrals

In this Section we consider integrals which are conveniently evaluated in ellipsoidal coordinates with the orbital centers as foci. These integrals are of the general form $\int \Psi_a^*(\mathbf{r}) \mathcal{O} \Psi_b(\mathbf{r})\, d\mathbf{r}$, with $\mathcal{O}$ standing for a multiplicative operator which, for the overlap integral is unity, and for the nuclear attraction integrals is r_a^{-1} or r_b^{-1} for nuclei at **A** or **B**, respectively. Consider two Slater-type orbitals Ψ_a and Ψ_b given in the form specified in Section II-A. We begin our analysis by making rotational transformations so that their individual polar axes point along the directed line from **A** to **B** and their $\phi = 0$ half-planes coincide. Letting $(\alpha_a^*, \beta_a^*, \gamma_a^*)$ and $(\alpha_b^*, \beta_b^*, \gamma_b^*)$ stand for the rotations of the axial systems at

A and **B** which accomplish this, the real orbital Ψ_a becomes a linear combination of complex orbitals, all with the l value l_a, but with a range of m values. In particular,

$$\Psi_a = \tfrac{1}{2} \sum_{\sigma=-l_a}^{l_a} [D_{l_a}^{m_a,\sigma_a}(\alpha_a^*, \beta_a^*, \gamma_a^*) + D_{l_a}^{-m_a,\sigma_a}(\alpha_a^*, \beta_a^*, \gamma_a^*)]$$
$$\times r_a^{n_a-1} \exp(-\delta_a r_a) P_{l_a}^{\sigma_a}(\cos\theta_a') \exp(i\sigma_a\phi), \quad m_a \geqslant 0; \quad (17a)$$

$$\Psi_a = \frac{1}{2i} \sum_{\sigma=-l_a}^{l_a} [D_{l_a}^{-m_a,\sigma_a}(\alpha_a^*, \beta_a^*, \gamma_a^*) - D_{l_a}^{m_a,\sigma_a}(\alpha_a^*, \beta_a^*, \gamma_a^*)]$$
$$\times r_a^{n_a-1} \exp(-\delta_a r_a) P_{l_a}^{\sigma_a}(\cos\theta_a') \exp(i\sigma_a\phi), \quad m_a < 0; \quad (17b)$$

where θ_a', ϕ are the angular coordinates in the rotated axial system about **A**. Similar equations may be written for Ψ_b. We write ϕ, rather than ϕ_a' or ϕ_b', because in the rotated axial systems the ϕ coordinates coincide and will also be used as the azimuthal ellipsoidal coordinate.

Using eq. (17) for Ψ_a^* and Ψ_b, and forming the integrals under consideration, we find that the ϕ integration leads to a zero result except for those combinations of terms for which $\sigma_a = -\sigma_b$. Since in that case the sign of σ_a is immaterial, we may observe that the integrals assume the general form

$$\int \Psi_a^*(\mathbf{r}) \mathcal{O} \Psi_b(\mathbf{r})\, d\mathbf{r} = \frac{R}{2} \sum_{\sigma=0}^{l_-} D_\sigma \int_{-1}^{1} d\eta \int_1^\infty d\xi r_a^{n_a}$$
$$\times \exp(-\delta_a r_a) P_{l_a}^{\sigma}(\cos\theta_a')\, \mathcal{O}\, r_b^{n_b} \exp(-\delta_b r_b) P_{l_b}^{\sigma}(\cos\theta_b'), \quad (18)$$

where l_- is the smaller of l_a and l_b, and D_σ is determined by making the substitutions indicated by eq. (17). We have converted the integration variables into ellipsoidal coordinates (ξ, η, ϕ) and have already integrated over ϕ. The volume element has been introduced in the form $d\mathbf{r} = \frac{1}{2} R r_a r_b\, d\xi\, d\eta\, d\phi$, where R stands for $|\mathbf{A} - \mathbf{B}|$.

Our next step is to complete the conversion into ellipsoidal coordinates. We note that explicit substitution for $\mathcal{O}$ either has no effect or decreases the exponent of r_a or r_b by unity. Writing $r_a^n \exp(-\delta_a r_a) P(\cos_{l_a}^{\sigma} \theta_a')$ as

$$[r_a^{n-l_a} \exp(-\delta_a r_a)] r_a^{l_a} P_{l_a}^{\sigma}(\cos\theta_a'),$$

where n is either n_a or $(n_a - 1)$, we convert the expression in square brackets by substituting $r_a = R(\xi + \eta)/2$. The remaining factor can be written as $\rho^{|\sigma|}$ times a homogeneous polynomial in r_a and z_a, of degree $l_a - |\sigma|$. Here

$$\rho = r_a \sin \theta'_a = \tfrac{1}{2}R[(\xi^2 - 1)(1 - \eta^2)]^{1/2}$$

and

$$z_a = r_a \cos \theta'_a = R(\xi\eta + 1)/2.$$

The corresponding expressions for Ψ_b involve $r_b = R(\xi - \eta)/2$ and $z_b = r_b \cos \theta'_b = R(\xi\eta - 1)/2$. The operations described here cause the integrand of eq. (18) to have an exponential dependence upon ξ and η, multiplied by a polynomial in ξ and η. The introduction of $\mathcal{O} = r_a^{-1}$ or r_b^{-1} does not lead to terms in the denominator because n_a and n_b must be at least unity. The integrals resulting from the complete conversion of eq. (18) into ellipsoidal coordinates therefore all have the general form

$$\int_{-1}^{1} d\eta \int_{1}^{\infty} d\xi \, \xi^p \eta^q \exp(-\delta\xi - \zeta\eta) = A_p(\delta) B_q(\zeta), \tag{19}$$

where $\delta = R(\delta_a + \delta_b)/2$, $\zeta = R(\delta_a - \delta_b)/2$, and $A_p(\delta)$ and $B_q(\zeta)$ are the well-known functions

$$A_p(\delta) = \int_{1}^{\infty} dt \, t^p e^{-\delta t} \tag{20}$$

and

$$B_q(\zeta) = \int_{-1}^{1} dt \, t^q e^{-\delta t}. \tag{21}$$

Generation of these functions is discussed in Appendix C.

It would be a tedious exercise to make and program the substitutions described in the foregoing paragraph for all possible combinations of the various quantum numbers. We have found it more expedient to program a computer directly to perform the algebraic manipulations here required, using coefficient arrays and algorithms based on the recurrence relations for the Legendre functions. This procedure is less efficient than explicit programming of formulae for each case, but in any event the integrals now under consideration consume a negligible fraction of the total computational effort involved in a complete molecular integral calculation.

B. Geometrical Considerations

In the preceding Section we saw that to evaluate the one-electron two-center integrals we needed to make rotations to align the orbital axes with a common ellipsoidal coordinate system. To carry out these and the other operations there described, we need means of determining the rotations $(\alpha_a^*, \beta_a^*, \gamma_a^*)$ and $(\alpha_b^*, \beta_b^*, \gamma_b^*)$, and also the distance $R = |\mathbf{A} - \mathbf{B}|$.

Our starting point is the coordinate data for **A** and **B**, namely, (R_a, Θ_a, Φ_a) and (R_b, Θ_b, Φ_b). Referring to Fig. 1, we see that

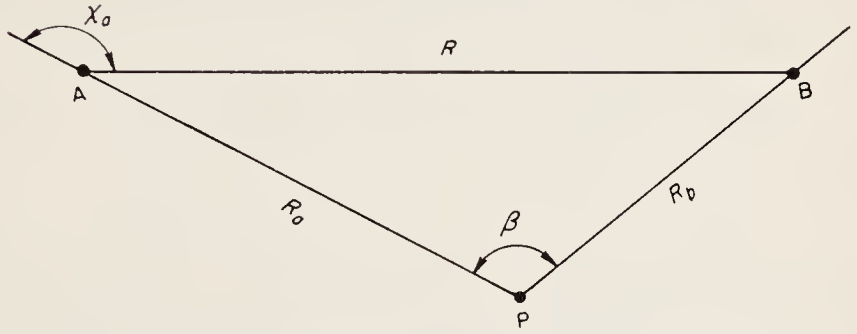

Fig. 1. Angular relationships involving ellipsoidal coordinate system with foci at **A** and **B**.

the angle β may be characterized as arising from a rotational transformation (α, β, γ) carrying the ray $\overline{PA}$ into the ray $\overline{PB}$, or,

$$(\alpha, \beta, \gamma)(\Phi_a, \Theta_a, 0) = (\Phi_b, \Theta_b, 0). \tag{22}$$

Then R may be calculated by using the law of cosines:

$$R^2 = R_a^2 + R_b^2 - 2R_aR_b \cos \beta. \tag{23}$$

Next we calculate the angle shown in Fig. 1 as χ_a, from the formula

$$\cos \chi_a = \frac{R_b \cos \beta - R_a}{R}. \tag{24}$$

This is the angle through which ray $\overline{PA}$ must be rotated to be oriented along the ray $\overline{AB}$. Some thought will permit one to see that the axial system $(\Phi_a, \Theta_a, 0)$ can be directed along ray $\overline{AB}$ by the transformation $(\alpha, \chi_a, 0)$, with α as given in eq. (22), since

the tilting of the axis to reach $\overline{AB}$ from $\overline{PA}$ must be at the same angle α as is necessary to reach $\overline{PB}$. The fact that the third Eulerian angle is zero means that after the rotation the point **P** is in the $\phi = 0$ half-plane.

The arguments of the preceding paragraph amount to the symbolic equation

$$(\alpha, \chi_a, 0)(\Phi_a, \Theta_a, 0) = (\overline{AB}), \tag{25}$$

where $(\overline{AB})$ indicates the orientation with polar axis along ray $\overline{AB}$. What we really need, however, are transformations carrying $(\alpha_a, \beta_a, \gamma_a)$ and $(\alpha_b, \beta_b, \gamma_b)$ into $(\overline{AB})$. In other words, we seek $(\alpha_a^*, \beta_a^*, \gamma_a^*)$ and $(\alpha_b^*, \beta_b^*, \gamma_b^*)$ such that

$$(\alpha_a^*, \beta_a^*, \gamma_a^*)(\alpha_a, \beta_a, \gamma_a) = (\alpha, \chi_a, 0)(\Phi_a, \Theta_a, 0) \tag{26}$$

and

$$(\alpha_b^*, \beta_b^*, \gamma_b^*)(\alpha_b, \beta_b, \gamma_b) = (\alpha, \chi_a, 0)(\Phi_a, \Theta_a, 0). \tag{27}$$

We solve these equations by using the analysis given in eqs. (12) and (13) to find the product $(\alpha, \chi_a, 0)(\Phi_a, \Theta_a, 0)$, after which eqs. (26) and (27) reduce to our standard computational form. In terms of the computational procedure ROT, the results of this Section take the form

CALL ROT $(\Phi_a, \Theta_a, 0, \Phi_b, \Theta_b, 0, \alpha, \beta, \gamma)$

Compute R from eq. (23)

Compute χ_a from eq. (24)

CALL ROT $(\pi, \Theta_a, \pi - \Phi_a, \alpha, \chi_a, 0, \alpha', \beta', \gamma')$

CALL ROT $(\alpha_a, \beta_a, \gamma_a, \alpha', \beta', \gamma', \alpha_a^*, \beta_a^*, \gamma_a^*)$

CALL ROT $(\alpha_b, \beta_b, \gamma_b, \alpha', \beta', \gamma', \alpha_b^*, \beta_b^*, \gamma_b^*)$

C. Kinetic Energy Integrals

The two previous Sections describe the evaluation of integrals involving multiplicative operators, such as the overlap and nuclear attraction integrals. The kinetic energy integrals, which are not of this type, can be evaluated by relating them to overlap integrals. Since we shall need to refer to overlap integrals with contiguous values of the quantum numbers, we introduce the alternate

notations $(n_a, l_a, m_a, \mathbf{A})$ for Ψ_a and $(n_a, l_a, m_a, \mathbf{A}|n_b, l_b, m_b, \mathbf{B})$ for S_{ab}.

Applying $-\nabla^2/2$ to Ψ_b in the form

$$-\frac{\nabla^2}{2} = -\frac{1}{2r_b^2}\frac{\partial}{\partial r_b}\left(r_b^2\frac{\partial}{\partial r_b}\right) + \frac{1}{2r_b^2}\mathscr{L}^2 \tag{28}$$

where $\mathscr{L}$ is the orbital angular momentum operator, and using the well-known relation

$$\mathscr{L}^2\Psi_b = l_b(l_b + 1)\Psi_b \tag{29}$$

(note that we use atomic units throughout), we obtain

$$\begin{aligned}-\frac{\nabla^2}{2}\Psi_b = &-\tfrac{1}{2}(n_b + l_b)(n_b - l_b - 1)(n_b - 2, l_b, m_b, \mathbf{B}) \\ &+ n_b\delta_b(n_b - 1, l_b, m_b, \mathbf{B}) - \tfrac{1}{2}\delta_b^2(n_b, l_b, m_b, \mathbf{B}).\end{aligned} \tag{30}$$

Upon multiplying by Ψ_a^* and integrating, we get the formula given by Roothaan (1951):

$$\begin{aligned}T_{ab} = &-\tfrac{1}{2}(n_b + l_b)(n_b - l_b - 1)(n_a, l_a, m_a, \mathbf{A}|n_b - 2, l_b, m_b, \mathbf{B}) \\ &+ n_b\delta_b(n_a, l_a, m_a, \mathbf{A}|n_b - 1, l_b, m_b, \mathbf{B}) \\ &- \tfrac{1}{2}\delta_b^2(n_a, l_a, m_a, \mathbf{A}|n_b, l_b, m_b, \mathbf{B}).\end{aligned} \tag{31}$$

Notice that the coefficients in eq. (31) do not depend upon the quantum number m, so that eq. (31) does not depend for its validity upon any particular relative orientation of the axial systems for Ψ_a and Ψ_b.

D. Special Cases

The only significant special case arises when the two centers **A** and **B** are actually the same center. We have found it convenient to avoid large quantities of special work for this case by evaluating the one-electron integrals in ellipsoidal coordinates with one focus at the common position of **A** and **B** and with the other focus at an arbitrary point at, say, a distance $R = 2$ along the positive polar axis of the original coordinate system for Ψ_a. This choice of axial system causes only contributions for $|\sigma_b| = |m_a|$ in the rotational transformation of Ψ_b into the Ψ_a axial system, thereby obtaining some of the benefits of the spherical symmetry about the common orbital center. The remaining condition arising

from the spherical symmetry, namely that the integrals here discussed all vanish unless $l_a = l_b$, can be explicitly examined before any other operations are carried out. After making these procedural adjustments, the steps already outlined will yield one-center integrals without introduction of new numerical procedures.

IV. THREE-CENTER NUCLEAR ATTRACTION INTEGRALS

A. Preliminary Reduction of Integrals

The three-center nuclear attraction integrals are evaluated in ellipsoidal coordinates by a method to be described elsewhere by the present authors (Michels and Harris). A previous study of this type of integral has been given by Hoyland (1964a, b) and Barnett (1963). The first step, just as for the two-center integrals, is to effect a rotational transformation on each orbital according to eq. (17), with the axial rotations determined as in Section III-B. However, in contrast to the situation discussed in Section III, the summations over σ_a and σ_b do not reduce to terms for which $\sigma_a = -\sigma_b$, because the nuclear attraction operator, in general, depends upon the ellipsoidal coordinate ϕ. Accordingly, the general three-center nuclear-attraction integral involving orbitals at **A** and **B**, and a nucleus at **C**, will be a linear combination of integrals which we may write as

$$\int \Psi_a^*(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{C}|} \Psi_b(\mathbf{r})\, d\mathbf{r} = \frac{R}{2} \sum_{\sigma_a=-l_a}^{l_a} \sum_{\sigma_b=-l_b}^{l_b} D_{\sigma_a,\sigma_b} \int_0^{2\pi} d\phi \int_{-1}^{1} d\eta \int_1^{\infty} d\xi$$

$$\times r^{n_a} e^{-\delta_a r_a} P_{l_a}^{\sigma_a}(\cos\theta_a') e^{-i\sigma_a\phi} \left(\frac{1}{|\mathbf{r} - \mathbf{C}|}\right) r_b^{n_b} e^{-\delta_b r_b} P_{l_b}^{\sigma_b}(\cos\theta_b') e^{i\sigma_b\phi}. \quad (32)$$

We now finish the conversion of eq. (32) into ellipsoidal coordinates by using the Neumann expansion of $1/|\mathbf{r} - \mathbf{C}|$ given in eq. (15) and the relationships given in Section III-A. Letting the ellipsoidal coordinates of **C** be (Ξ, H, Φ), we find, after integration over the ϕ coordinate, that the right side of eq. (32) reduces to a sum of terms:

$$\int \Psi_a^*(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{C}|} \Psi_b(\mathbf{r})\, d\mathbf{r} = \sum_{\mu=0}^{\infty} \sum_{\nu=-\mu}^{\mu} \sum_{p,q} B_{\mu pq}^{\nu} Z_{\mu pq}^{\nu}(\Xi, H, \Phi), \quad (33)$$

where

$$Z^{\nu}_{\mu pq}(\Xi, \mathrm{H}, \Phi) = \left[\frac{(\mu - |\nu|)!}{(\mu + |\nu|)!}\right]^2 P^{\nu}_{\mu}(\mathrm{H}) e^{i\nu\Phi} \int_{-1}^{1} \mathrm{d}\eta \int_{1}^{\infty} \mathrm{d}\xi$$
$$\times \xi^{p}\eta^{q}[(\xi^2 - 1)(1 - \eta^2)]^{|\nu|/2} e^{-\delta\xi - \zeta\eta} P^{\nu}_{\mu}(\eta) P^{\nu}_{\mu}(\xi_{-}) Q^{\nu}_{\mu}(\xi_{+}) \quad (34)$$

with $\delta = R(\delta_a + \delta_b)/2$, $\zeta = R(\delta_a - \delta_b)/2$, and ξ_+ and ξ_- the greater and lesser, respectively, of ξ and Ξ. In eq. (33), the sums over p and q are finite with ranges determined by the quantum numbers of Ψ^{*}_{a} and Ψ_{b}. The sums over μ and ν arise from the Neumann expansion and have the limits indicated. Just as for the two-center integrals, it is extremely tedious to determine the coefficients $B^{\nu}_{\mu pq}$ for all possible combinations of the quantum numbers, so the necessary algebraic algorithms for defining these coefficients were programmed.

To complete the evaluation of the three-center nuclear attraction integrals we require simplified expressions for the integral $Z^{\nu}_{\mu pq}(\Xi, \mathrm{H}, \Phi)$. We proceed by factoring the integral into separate integrations over the variables ξ and η, and then by breaking the range of the ξ integration into the two parts $\xi < \Xi$ and $\xi > \Xi$. The result is

$$Z^{\nu}_{\mu pq}(\Xi, \mathrm{H}, \Phi) = P^{\nu}_{\mu}(\mathrm{H}) e^{i\nu\Phi} I^{\nu}_{pq}(\zeta)[P^{\nu}_{\mu}(\Xi) L^{\nu}_{\mu p}(\Xi, \delta) + Q^{\nu}_{\mu}(\Xi) K^{\nu}_{\mu p}(\Xi, \delta)], \quad (35)$$

where

$$I^{\nu}_{\mu q}(\zeta) = \frac{(\mu - |\nu|)!}{(\mu + |\nu|)!} \int_{-1}^{1} e^{-\zeta\eta}\eta^{q} P^{\nu}_{\mu}(\eta)(1 - \eta^2)^{|\nu|/2}\, \mathrm{d}\eta, \quad (36)$$

$$K^{\nu}_{\mu p}(\Xi, \delta) = \frac{(\mu - |\nu|)!}{(\mu + |\nu|)!} \int_{1}^{\Xi} e^{-\delta\xi}\xi^{p} P^{\nu}_{\mu}(\xi)(\xi^2 - 1)^{|\nu|/2}\, \mathrm{d}\xi, \quad (37)$$

and

$$L^{\nu}_{\mu p}(\Xi, \delta) = \frac{(\mu - |\nu|)!}{(\mu + |\nu|)!} \int_{\Xi}^{\infty} e^{-\delta\xi}\xi^{p} Q^{\nu}_{\mu}(\xi)(\xi^2 - 1)^{|\nu|/2}\, \mathrm{d}\xi. \quad (38)$$

The integrals $I^{\nu}_{\mu q}(\zeta)$ and $K^{\nu}_{\mu p}(\Xi, \delta)$ also occur in the ellipsoidal expansion of two-center electron repulsion integrals and have been extensively studied (see, for example, Kotani and his colleagues, 1955, and Harris, 1960). The evaluation of the integral

$I^{\nu}_{\mu q}(\zeta)$ is discussed in Appendix C, while the integrals $K^{\nu}_{\mu p}(\Xi, \delta)$ and $L^{\nu}_{\mu p}(\Xi, \delta)$ are evaluated in Appendix D.

B. Determination of Nuclear Coordinates (Ξ, H, Φ)

The nuclear coordinates Ξ and H are easily calculated from the distances $R_{ac} = |\mathbf{A} - \mathbf{C}|$ and $R_{bc} = |\mathbf{B} - \mathbf{C}|$:

$$\Xi = (R_{ac} + R_{bc})/R, \tag{39}$$

and

$$\mathrm{H} = (R_{ac} - R_{bc})/R. \tag{40}$$

The distances R_{ac} and R_{bc}, in turn, are obtained from R_a, R_b, R_c, and the angles $\beta_{ac} = \angle APC$ and $\beta_{bc} = \angle BPC$:

$$R^2_{ac} = R^2_a + R^2_c - 2R_aR_c \cos \beta_{ac}, \tag{41}$$

and

$$R^2_{bc} = R^2_b + R^2_c - 2R_bR_c \cos \beta_{bc}. \tag{42}$$

The angles β_{ac} and β_{bc} satisfy the relations

$$(\alpha_{ac}, \beta_{ac}, \gamma_{ac})(\Phi_a, \Theta_a, 0) = (\Phi_c, \Theta_c, 0) \tag{43}$$

$$(\alpha_{bc}, \beta_{bc}, \gamma_{bc})(\Phi_b, \Theta_b, 0) = (\Phi_c, \Theta_c, 0). \tag{44}$$

The nuclear coordinate Φ may be obtained by considering the axial transformation needed to go from the coordinate system $(\overline{AB})$ to a system with polar axis along the ray $\overline{AC}$. The first Eulerian angle of this transformation is Φ, and symbolically we have

$$(\Phi, x, x')(\overline{AB}) = (\overline{AC}). \tag{45}$$

In Section III-B we determined the transformations necessary to specify the orientation of $(\overline{AB})$. Similar operations lead to a determination of $(\overline{AC})$, following which eq. (45) can be used to obtain Φ.

A procedural description of the operations discussed above is the following:

Compute $(\alpha', \beta', \gamma')$ by procedure of Section III-B
CALL ROT $(\Phi_a, \Theta_a, 0, \Phi_c, \Theta_c, 0, \alpha_{ac}, \beta_{ac}, \gamma_{ac})$
CALL ROT $(\Phi_b, \Theta_b, 0, \Phi_c, \Theta_c, 0, \alpha_{bc}, \beta_{bc}, \gamma_{bc})$
Compute R_{ac} and R_{bc} from eqs. (41) and (42)

Compute χ_{ac} from $\chi_{ac} = (R_c \cos \beta_{ac} - R_a)/R_{ac}$
CALL ROT $(\pi, \Theta_a, \pi - \Phi_a, \alpha_{ac}, \chi_{ac}, 0, \alpha'', \beta'', \gamma'')$
CALL ROT $(\alpha', \beta', \gamma', \alpha'', \beta'', \gamma'', \Phi, x, x')$

C. SPECIAL CASES

Special cases result if the nuclear position **C** is on the line defined by the orbital centers **A** and **B**. In this event, all terms of eq. (33) vanish except those for which $\nu = 0$. If **C** lies on the line defined by **A** and **B**, but is not between them, we have $H = \pm 1$, so that the factor $P_\mu(H)$ becomes $(\pm 1)^\mu$, and eq. (35) reduces to

$$Z_{\mu pq}(\Xi, \pm 1, \Phi) = (\pm 1)^\mu I_{\mu q}(\zeta)[P_\mu(\Xi)L_{\mu p}(\Xi, \delta) + Q_\mu(\Xi)K_{\mu p}(\Xi, \delta)]. \tag{46}$$

If **C** lies between **A** and **B**, then $\Xi = 1$ and eq. (35) becomes an indeterminate form because as $\Xi \to 1+$, $Q_\mu(\Xi) \to \infty$, while $K_{\mu p}(\Xi, \delta) \to 0$. However, the product $Q_\mu(\Xi)K_{\mu p}(\Xi, \delta)$ approaches zero because $Q_\mu(\Xi)$ diverges logarithmically while $K_{\mu p}(\Xi, \delta)$ vanishes linearly. Noting that $L_{\mu p}(\Xi, \delta)$ is defined at $\Xi \to 1+$, we have the limit

$$Z_{\mu pq}(1, H, \Phi) = P_\mu(H)I_{\mu q}(\zeta)L_{\mu p}(1, \delta). \tag{47}$$

The evaluation of $L_{\mu p}(1, \delta)$ is described in Appendix D.

V. ELECTRON REPULSION INTEGRALS

A. One-Center Integrals

One-center electron-repulsion integrals are easily evaluated in a spherical coordinate system. The first step is to express each charge distribution as a spherical harmonic expansion about the common center of both charge distributions, using the same axial orientation for both distributions:

$$\Psi_a^*(\mathbf{r}_1)\Psi_b(\mathbf{r}_1) = r_1^{n_1-2}e^{-\delta_1 r_1}\sum_\mu\sum_\nu F_{\mu,\nu}^{ab}P_\mu^\nu(\cos\theta_1)e^{i\nu\phi_1} \tag{48a}$$

and

$$\Psi_c^*(\mathbf{r}_2)\Psi_d(\mathbf{r}_2) = r_2^{n_2-2}e^{-\delta_2 r_2}\sum_\mu\sum_\nu F_{\mu,\nu}^{cd}P_\mu^\nu(\cos\theta_2)e^{i\nu\phi_2}. \tag{48b}$$

Here $\delta_1 = \delta_a + \delta_b$, $\delta_2 = \delta_c + \delta_d$, $n_1 = n_a + n_b$, and $n_2 = n_c + n_d$. The evaluation of $F^{ab}_{\mu,\nu} F^{cd}_{\mu,\nu}$ will be discussed below. The sums over μ and ν have finite limits determined by the orbitals involved. In any case, μ cannot exceed $(n_1 - 2)$ or $(n_2 - 2)$, for eqs. (48a) and (48b), respectively.

The next step is to form the electron-repulsion integral, using eq. (14) to expand $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$. On use of the orthogonality relations for the Legendre functions, given in Appendix B, the expansion of the one-center electron repulsion integral reduces to:

$$X_{ab,cd} = \int \Psi_a^*(\mathbf{r}_1)\Psi_b(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \Psi_c^*(\mathbf{r}_2)\Psi_d(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2$$

$$= \sum_l \sum_m \left(\frac{4\pi}{2l+1}\right)^2 \frac{(l + |m|)!}{(l - |m|)!} F^{ab}_{l,m} F^{cd}_{l,-m}$$

$$\int_0^\infty dr_1 \int_0^\infty dr_2 \frac{r_-^l}{r_+^{l+1}} r_1^{n_1} r_2^{n_2} e^{-\delta_1 r_1 - \delta_2 r_2}, \quad (49)$$

where r_- and r_+ are the lesser and greater, respectively, of r_1 and r_2. The limits of the l and m summations are determined by those in eqs. (48a) and (48b), so that l cannot exceed the lesser of $n_1 - 2$ and $n_2 - 2$.

We continue with the evaluation of eq. (49) by breaking the integration into parts for which $r_1 < r_2$ and $r_1 > r_2$. Introducing the auxiliary function

$$S(i, j, \alpha) = \int_0^\infty x^i e^{-\alpha x} A_j(x)\, dx, \quad (50)$$

where $A_j(x)$ is as given in eq. (20), eq. (49) assumes the form

$$X_{ab,cd} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \left(\frac{4\pi}{2l+1}\right)^2 \frac{(l + |m|)!}{(l - |m|)!} F^{ab}_{l,m} F^{cd}_{l,-m}$$

$$\times [\delta_1^{-n_1-n_2-1} S(n_1 + n_2, n_1 - l - 1, \delta_2/\delta_1)$$

$$+ \delta_2^{-n_1-n_2-1} S(n_1 + n_2, n_2 - l - 1, \delta_1/\delta_2)]. \quad (51)$$

The auxiliary function $S(i, j, \alpha)$ may be generated recursively by the introduction into eq. (50) of the recurrence relation for $A_j(x)$, which is given in Appendix C. We find

$$S(i, j, \alpha) = jS(i - 1, j - 1, \alpha) + S(i, 0, \alpha). \quad (52)$$

Starting values are provided by the direct integration of $S(i, 0, \alpha)$, which yields

$$S(i, 0, \alpha) = (i - 1)!(\alpha + 1)^{-i}. \tag{53}$$

The limitation on the range of l values causes $S(i, j, \alpha)$ to be needed only for $0 \leqslant j \leqslant i - 2$ and for $i \geqslant 4$. This means that all the required values of $S(i, j, \alpha)$ can be obtained by use of eqs. (52) and (53).

The remaining problem is that of producing the coefficients $F^{ab}_{\mu,\nu}$ and $F^{cd}_{\mu,\nu}$. This can be accomplished in two steps. We first bring the axes of the individual orbitals into coincidence, and then multiply together the orbitals forming each charge distribution. The axial rotations have already been described in earlier sections of this study. Rotating each axial system so that it is aligned parallel to the common space-fixed axes, each orbital is described by an expansion similar to eq. (17a) or (17b), but with angular coordinates (θ_1, ϕ_1) or (θ_2, ϕ_2) in the space-fixed system. The rotational transformation needed to reach this alignment is, for Ψ_a, the inverse of that defined by $(\alpha_a, \beta_a, \gamma_a)$, namely $(\pi - \gamma_a, \beta_a, \pi - \alpha_a)$. Corresponding rotations are then applied to Ψ_b, Ψ_c, and Ψ_d.

After the axial rotations, each charge distribution can be written as a sum of products involving pairs of spherical harmonics. These products are reduced using the Clebsch–Gordan expansion, which we take in the form

$$P^m_l(x) P^{m'}_{l'}(x) = \sum_j C^{mm'}_{jll'} P^{m+m'}_j(x). \tag{54}$$

The methods used to generate the Clebsch–Gordan coefficients $C^{mm'}_{jll'}$ are discussed in Appendix B. Application of the rotational transformations and eq. (54) lead in a straightforward but tedious manner to the coefficients appearing in eqs. (48). As in earlier parts of this work, we programmed a computer to perform the indicated algebraic details.

B. Convolution Methods for Coulomb-type Integrals

The convolution methods that we describe in the present Section have been found to be more convenient, and computationally faster than application of the more general techniques which are described in subsequent Sections. In their simplest form,

convolution methods are only applicable to Coulomb-type integrals. The starting point for Coulomb-type integrals is the expansion of each charge distribution in spherical harmonics about its center, in forms such as eqs. (48a) and (48b). As we shall see below, it is convenient to make the expansions in terms of coordinate systems with polar axes aligned along the line of the two centers, which we designate as **A** and **B**. The axial rotations needed to accomplish this alignment are discussed in Section III-B. After the rotational transformations have been made, a Coulomb-type integral can be written as

$$X_{ab,cd} = \sum_{l,l'} \sum_{m} F^{ab}_{l,m} F^{cd}_{l',-m} \int d\mathbf{r}_1\, d\mathbf{r}_2\, r_{1A}^{n_1} r_{2B}^{n_2} e^{-\delta_1 r_{1A} - \delta_2 r_{2B}} \times P_l^m(\cos\theta_{1A}) P_{l'}^m(\cos\theta_{2B}) e^{im(\phi_1 - \phi_2)} \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}. \tag{55}$$

Here the cylindrical symmetry has permitted the simplification to a single summation over m. The evaluation of the coefficients $F^{ab}_{l,m}$ and $F^{cd}_{l',-m}$ has been described previously, and the remainder of this Section is directed toward the evaluation of the integral appearing in eq. (55). We simplify the discussion by introducing ϕ_A and ϕ_B to stand for $r_{1A}^{n_1} P_l^m(\cos\theta_{1A}) \exp(-\delta_1 r_{1A} + im\phi_1)$ and $r_{2B}^{n_2} P_{l'}^m(\cos\theta_{2B}) \exp(-\delta_2 r_{2B} - im\phi_2)$.

The integral in eq. (55) is then

$$C = \int \phi_A(\mathbf{r}_{1A}) \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} \phi_B(\mathbf{r}_{2B})\, d\mathbf{r}_1\, d\mathbf{r}_2. \tag{56}$$

The integral C may be simplified by application of the Fourier convolution theorem. This theorem enables each of the integral's one-center charge distributions to be handled in terms of coordinates about the distribution's own center. Invoking the parity of the Legendre functions and the relation $\mathbf{r}_{2B} = \mathbf{r}_{2A} - \mathbf{B} + \mathbf{A}$, we may write $\phi_B(\mathbf{r}_{2B}) = (-1)^{l'}\phi_B(-\mathbf{r}_{2B}) = (-1)^{l'}\phi_B(\mathbf{R} - \mathbf{r}_{2A})$, where $\mathbf{R} = \mathbf{B} - \mathbf{A}$. Then the integral C becomes

$$C = (-1)^{l'} \int d\mathbf{r}_{1A}\, d\mathbf{r}_{2A}\, \phi_A(\mathbf{r}_{1A}) V(\mathbf{r}_{2A} - \mathbf{r}_{1A}) \phi_B(\mathbf{R} - \mathbf{r}_{2A}), \tag{57}$$

where $V(\mathbf{r})$ is, in the current application, the Coulomb potential r_{12}^{-1}. Equation (57) shows that C, regarded as a function of $\mathbf{R}$, has according to the convolution theorem the Fourier transform

$\phi_A^T(\mathbf{k})V^T(\mathbf{k})\phi_B^T(\mathbf{k})$, where $\mathbf{k}$ is the transform variable and the superscript T indicates the Fourier transform. We then apply the Fourier inversion theorem to obtain the result

$$C = \frac{(-1)^{l'}}{(2\pi)^3}\int e^{-i\mathbf{k}\cdot\mathbf{R}}\phi_A^T(\mathbf{k})V^T(\mathbf{k})\phi_B^T(\mathbf{k})\,d\mathbf{k}. \tag{58}$$

Equation (58) may be reduced to a more useful form by introducing the Fourier transforms of the factors in the integrand. Using polar coordinates $(k, \bar{\theta}, \bar{\phi})$ for $\mathbf{k}$, $V^T(\mathbf{k}) = 4\pi k^{-2}$. In terms of the alternate notations (n_1, l, m, δ_1) for ϕ_A and $(n_2, l', -m, \delta_2)$ for ϕ_B,

$$(n, l, m, \delta)^T = 4\pi i^l (n, l, \delta)^T P_l^m(\cos\bar{\theta})e^{im\bar{\phi}}, \tag{59}$$

where

$$(n, l, \delta)^T = \int_0^\infty r^{n+2} j_l(kr)e^{-\delta r}\,dr. \tag{60}$$

The spherical Bessel function $j_l(x)$ is described in Appendix C. After substitution of these Fourier transforms, the integral C becomes

$$C = 8i^{l-l'}\int e^{-i\mathbf{k}\cdot\mathbf{R}}(n_1, l, \delta_1)^T(n_2, l', \delta_2)^T \times P_l^m(\cos\bar{\theta})P_{l'}^m(\cos\bar{\theta})k^{-2}\,d\mathbf{k}. \tag{61}$$

When the Clebsch–Gordan series given in eq. (54) is used for the product of Legendre functions, with the expansion of $\exp(-i\mathbf{k}\cdot\mathbf{R})$, given in eq. (16), eq. (61) may be written:

$$C = \sum_L A_{Ll'}^m \cdot \frac{2}{\pi}\int_0^\infty j_L(kR)(n_1, l, \delta_1)^T(n_2, l', \delta_2)^T\,dk \tag{62}$$

with

$$A_{Ll'}^m = 16\pi^2 i^{l-l'-L}C_{Ll'}^{m,-m} \tag{63}$$

and where the polar axis for $\mathbf{k}$ is taken to be in the $+\mathbf{R}$ direction. Equation (62) is essentially the result obtained by Geller (1964a, b).

Our next task is to obtain explicit expressions for the transforms $(n, l, \delta)^T$. We found it convenient to generate these recursively, using recurrence relations obtained by applying either partial integrations or Bessel function identities to eq. (60). Some of these recurrence relations are given in Appendix E. From the recurrence relations, or alternatively from the general formula

given by Geller (1964a, b), it is clear that the $(n, l, \delta)^T$ have the general form

$$(n, l, \delta)^T = k^l \sum_{i \geq (n+l+3)/2}^{n+2} B_{n,l,i}(k^2 + \delta^2)^{-i}. \tag{64}$$

The $B_{n,l,i}$ may be generated from the relations

$$B_{-1,0,1} = 1; \tag{65}$$

$$B_{l-1,l,l+1} = 2lB_{l-2,l-1,l}; \tag{66}$$

$$B_{l,l,l+2} = (2l + 2)B_{l-1,l,l+1}; \tag{67}$$

$$B_{n,l,i} = 2(n + 1)B_{n-1,l,i-1} - (n + l + 1)(n - l)B_{n-2,l,i-1}. \tag{68}$$

Equations (65)–(68) are consequences of the recurrence relations given in Appendix E.

Substitution of eq. (64) into eq. (62) leads to

$$C = \sum_L \sum_{i,i'} A^m_{Ll'} B_{n_1,l,i} B_{n_2,l',i'} W^{L,(l+l'-L)/2}_{i,i'}(\delta_1, \delta_2, R) \tag{69}$$

with

$$W^{L,j}_{i,i'}(\delta_1, \delta_2, R) = \frac{2}{\pi} \int_0^\infty \frac{k^{L+2j} j_L(kR)\, \mathrm{d}k}{(k^2 + \delta_1^2)^i (k^2 + \delta_2^2)^{i'}}. \tag{70}$$

The value of j needed in eq. (69), $\frac{1}{2}(l + l' - L)$, accounts for the power of k resulting from the introduction of eq. (64) for (n_1, l, δ_1) and (n_2, l', δ_2).

The remaining problem is the evaluation of eq. (70), which we accomplish by methods somewhat different than those suggested by Geller (1964a, b). First, we collect a few relations connecting W functions of contiguous index values. Using the identity $k^2/(k^2 + \delta_1^2) = 1 - \delta_1^2/(k^2 + \delta_1^2)$, we have

$$\delta_1^2 W^{L,j}_{i,i'} = W^{L,j}_{i-1,i'} - W^{L,j+1}_{i,i'} \tag{71}$$

and

$$\delta_2^2 W^{L,j}_{i,i'} = W^{L,j}_{i,i'-1} - W^{L,j+1}_{i,i'}. \tag{72}$$

Using the recurrence relation for j_L, we also have

$$\left(\frac{2L + 1}{R}\right) W^{L,j}_{i,i'} = W^{L+1,j}_{i,i'} + W^{L-1,j+1}_{i,i'}. \tag{73}$$

Equations (71)–(73) were reported by Geller (1964b). Further useful relations may be obtained by combining eqs. (71) and (72):

$$(\delta_2^2 - \delta_1^2) W_{i,i'}^{L,j} = W_{i,i'-1}^{L,j} - W_{i-1,i'}^{L,j}, \tag{74}$$

or by combining eqs. (71) and (73):

$$W_{i,i'}^{L+1,j} = \left(\frac{2L+1}{R}\right) W_{i,i'}^{L,j} - W_{i-1,i'}^{L-1,j} + \delta_1^2 W_{i,i'}^{L-1,j}. \tag{75}$$

In certain cases the $W_{i,i'}^{L,j}$ may be evaluated by direct quadrature. In particular, $W_{1,0}^{0,0}$ is simply (Gröbner and Hofreiter, 1958a)

$$\begin{aligned} W_{1,0}^{0,0} &= \frac{2}{\pi} \int_0^\infty \frac{\sin kR \, \mathrm{d}k}{kR(k^2 + \delta_1^2)} \\ &= \frac{1}{\delta_1^2 R} (1 - \mathrm{e}^{-\delta_1 R}). \end{aligned} \tag{76}$$

We also note the important result (Gröbner and Hofreiter, 1958b)

$$\begin{aligned} W_{i,0}^{L,1} &= \left(\frac{2}{\pi R}\right)^{\frac{1}{2}} \int_0^\infty \frac{k^{L+3/2} J_{L+1/2}(kR) \, \mathrm{d}k}{(k^2 + \delta_1^2)^i} \\ &= \frac{\delta_1^{L+1}}{(i-1)!} \left(\frac{R}{2\delta_1}\right)^{i-1} \left(\frac{2}{\pi \delta_1 R}\right)^{\frac{1}{2}} K_{i-L-3/2}(\delta_1 R). \end{aligned} \tag{77}$$

The Bessel functions in eq. (77) are defined in Appendix C. Corresponding to eqs. (75)–(77) is a set of equations in which i and i', and δ_1 and δ_2, are reversed.

Our procedure for generating the $W_{i,i'}^{L,j}$ is to make first $W_{i,i'}^{0,0}$ and $W_{i,i'}^{1,0}$ for a sufficient range of i and i', and then to use eq. (75) to advance L, and either eq. (71) or (72) to advance j if necessary. The construction of $W_{i,i'}^{0,0}$ and $W_{i,i'}^{1,0}$ depends upon the values of δ_1 and δ_2, and we distinguish three cases which we discuss below.

If δ_1/δ_2 is not too near unity, eq. (74) is a numerically satisfactory way of obtaining $W_{i,i'}^{L,j}$ from $W_{i-1,i'}^{L,j}$ and $W_{i,i'-1}^{L,j}$ and all $W_{i,i'}^{0,0}$ and $W_{i,i'}^{1,0}$ can be obtained by successive applications of eq. (74) to $W_{i,0}^{0,0}$, $W_{0,i'}^{0,0}$, $W_{i,0}^{1,0}$, and $W_{0,i'}^{1,0}$. The functions $W_{i,0}^{0,0}$ are generated by use of eq. (71), which in this case becomes

$$W_{i,0}^{0,0} = \delta_1^{-2}(W_{i-1,0}^{0,0} - W_{i,0}^{0,1}). \tag{78}$$

To use eq. (78) we need $W_{1,0}^{0,0}$, given by eq. (76), as a starting value, and the values of $W_{i,0}^{0,1}$, which are a special case of eq. (77):

$$W_{i,0}^{0,1} = \delta_1 \left(\frac{R}{2\delta_1}\right)^{i-1} \frac{k_{i-2}(\delta_1 R)}{(i-1)!}. \tag{79}$$

The $W_{i,0}^{1,0}$ may be made by eq. (73):

$$W_{i,0}^{1,0} = R^{-1} W_{i,0}^{0,0} - W_{i,0}^{-1,0}. \tag{80}$$

The $W_{i,0}^{0,0}$ needed for eq. (80) are to be made first, and the $W_{i,0}^{-1,1}$ are obtained from eq. (77), which yields

$$W_{i,0}^{-1,1} = \left(\frac{R}{2\delta_1}\right)^{i-1} \frac{k_{i-1}(\delta_1 R)}{(i-1)!}. \tag{81}$$

Corresponding operations lead to $W_{0,i'}^{0,0}$ and $W_{0,i'}^{1,0}$. The k_i are calculated by methods described in Appendix C.

If δ_1/δ_2 is near unity, eq. (74) becomes unsatisfactory, and the $W_{i,i'}^{0,0}$ and $W_{i,i'}^{1,0}$ must be generated by a method other than that outlined above. Our solution to this problem is first to make $W_{i,0}^{0,0}$ and $W_{i,0}^{1,0}$ according to eqs. (78)–(80), but then to use eq. (74) to go *down* in the index i, that is, to calculate $W_{i-1,i'}^{L,j}$ from $W_{i,i'}^{L,j}$ and $W_{i,i'-1}^{L,j}$. This approach enables calculation of $W_{i,i'}^{L,j}$ for a range of i from the set of $W_{i,i'-1}^{L,j}$, provided that $W_{i,i'}^{L,j}$ is available for the maximum relevant i value. Noting that successive applications of eq. (74) in this way cause an attenuation of any error in the initial $W_{i,i'}^{L,j}$, we start with $W_{I,i'}^{L,j} = 0$ for a value of I sufficiently large that, by the time I has been reduced to a value of interest the $W_{i,i'}^{L,j}$ are of acceptable accuracy. In practice it is found that it is not necessary to use unreasonably large I values.

If δ_1 and δ_2 are equal, the procedure of the foregoing paragraph, though acceptable, is unnecessarily complicated because then $W_{i,i'}^{L,j} = W_{i+i',0}^{L,j}$, and every $W_{i,i'}^{L,j}$ can be obtained directly from eqs. (77) and (71).

We note that previous formulations for Coulomb-type integrals (Roothaan, 1951; Geller, 1964b) do not distinguish the important case where δ_1/δ_2 is near unity and are, therefore, computationally unsatisfactory for such integrals.

C. Ellipsoidal Expansions for Two-center Integrals

Two-center integrals other than those of Coulomb-type cannot conveniently be calculated by the methods of the preceding Section. The general two-center integral may, however, be treated in ellipsoidal coordinates with the centers as foci (Harris, 1960). Introducing ellipsoidal coordinates as discussed in Sections III-A and IV-A, we write the two-center integral in the form

$$\mathcal{N}_{ab,cd} = \frac{R^2}{4}\int r_{1A}r_{1B}\Psi_a^*(\mathbf{r}_1)\Psi_b(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}r_{2A}r_{2B}\Psi_c^*(\mathbf{r}_2)\Psi_d(\mathbf{r}_2) \times d\xi_1\,d\xi_2\,d\eta_1\,d\eta_2\,d\phi_1\,d\phi_2. \quad (82)$$

We next expand the factors depending upon individual electrons as follows:

$$r_{1A}r_{1B}\Psi_a^*(\mathbf{r}_1)\Psi_b(\mathbf{r}_1) = \sum_{p,q,\nu} B_{p,q,\nu}^{ab}\xi_1^p\eta_1^q[(\xi_1^2-1)(1-\eta_1^2)]^{|\nu|/2}\,e^{-\delta_1\xi_1-\zeta_1\eta_1+i\nu\phi_1} \quad (83)$$

and

$$r_{2A}r_{2B}\Psi_c^*(\mathbf{r}_2)\Psi_d(\mathbf{r}_2) = \sum_{p,q,\nu} B_{p,q,\nu}^{cd}\xi_2^p\eta_2^q[(\xi_2^2-1)(1-\eta_2^2)]^{|\nu|/2}\,e^{-\delta_2\xi_2-\zeta_2\eta_2+i\nu\phi_2}. \quad (84)$$

Here $\delta_1 = R(\delta_a+\delta_b)/2$, $\delta_2 = R(\delta_c+\delta_d)/2$, $\zeta_1 = R(\delta_a-\delta_b)/2$, $\zeta_2 = R(\delta_c-\delta_d)/2$, **A** and **B** are the two centers, and $R = |\mathbf{B}-\mathbf{A}|$. When the Neumann expansion, eq. (15), is used for $|\mathbf{r}_1-\mathbf{r}_2|^{-1}$, and the integrations are carried out over ϕ_1 and ϕ_2, eq. (82) becomes

$$\mathcal{N}_{ab,cd} = 2\pi^2 R\sum_{\mu,\nu}(2\mu+1)\frac{(\mu+|\nu|)!}{(\mu-|\nu|)!}\sum_{p,q}\sum_{p',q'}B_{p,q,\nu}^{ab}B_{p',q',-\nu}^{cd}Z_{\mu pqp'q'}^{\nu}, \quad (85)$$

where

$$Z_{\mu pqp'q'}^{\nu} = (-1)^{\nu}\left[\frac{(\mu-|\nu|)!}{(\mu+|\nu|)!}\right]^3\int\xi_1^p\xi_2^{p'}\eta_1^q\eta_2^{q'}\,e^{-\delta_1\xi_1-\delta_2\xi_2-\zeta_1\eta_1-\zeta_2\eta_2} \times[(\xi_1^2-1)(1-\eta_1^2)(\xi_2^2-1)(1-\eta_2^2)]^{|\nu|/2} \times Q_\mu^\nu(\xi_+)P_\mu^\nu(\xi_-)P_\mu^\nu(\eta_1)P_\mu^\nu(\eta_2)\,d\xi_1\,d\xi_2\,d\eta_1\,d\eta_2. \quad (86)$$

Here ξ_+ and ξ_- are the greater and lesser, respectively, of ξ_1 and ξ_2. The coefficients $B_{p,q,\nu}^{ab}$ and $B_{p',q',-\nu}^{cd}$ are tedious to determine

for all possible combinations of the quantum numbers and are therefore more easily computed from simple algebraic algorithms.

The integral $Z^{\nu}_{\mu pqp'q'}$ can be simplified by factoring it into one-dimensional integrals to the extent that this is possible. Identifying the integrations over η_1 and η_2 as the function $I^{\nu}_{\mu q}$ defined at eq. (36), we have

$$Z^{\nu}_{\mu pqp'q'} = (-1)^{\nu} \frac{(\mu - |\nu|)!}{(\mu + |\nu|)!} I^{\nu}_{\mu q}(\zeta_1) I^{\nu}_{\mu q'}(\zeta_2) \int_1^{\infty} d\xi_1 \int_1^{\infty} d\xi_2 \times \xi_1^{p} \xi_2^{p'} e^{-\delta_1 \xi_1 - \delta_2 \xi_2} [(\xi_1^2 - 1)(\xi_2^2 - 1)]^{|\nu|/2} Q^{\nu}_{\mu}(\xi_+) P^{\nu}_{\mu}(\xi_-). \quad (87)$$

To separate further the integrations over ξ_1 and ξ_2 we use an integral transformation formula (Rüdenberg, 1951; Harris, 1960). The integral in eq. (87) is of the general form

$$I = \int_1^{\infty} dx \frac{Q^{\nu}_{\mu}(x)}{P^{\nu}_{\mu}(x)} \left[\phi_1(x) \int_1^{x} dz \, \phi_2(z) + \phi_2(x) \int_1^{x} dy \, \phi_1(y) \right], \quad (88)$$

where

$$\phi_1(x) = x^{p} e^{-\delta_1 x} (x^2 - 1)^{|\nu|/2} P^{\nu}_{\mu}(x)$$

and

$$\phi_2(x) = x^{p'} e^{-\delta_2 x} (x^2 - 1)^{|\nu|/2} P^{\nu}_{\mu}(x).$$

Alternatively, we can write

$$I = \int_1^{\infty} dx \frac{Q^{\nu}_{\mu}(x)}{P^{\nu}_{\mu}(x)} \frac{d}{dx} \left[\int_1^{x} dy \, \phi_1(y) \int_1^{x} dz \, \phi_2(z) \right] \quad (89)$$

and then integrate by parts. The form of ϕ_1 and ϕ_2 assure that the terms arising from the limits of the integration vanish, so that the result of the partial integration is

$$I = -\int_1^{\infty} dx \left[\frac{d}{dx} \left(\frac{Q^{\nu}_{\mu}(x)}{P^{\nu}_{\mu}(x)} \right) \right] \int_1^{x} dy \, \phi_1(y) \int_1^{x} dz \, \phi_2(z). \quad (90)$$

Now $\frac{d}{dx} [Q^{\nu}_{\mu}(x)/P^{\nu}_{\mu}(x)]$ is related to the Wronskian of P^{ν}_{μ} and Q^{ν}_{μ} and, as indicated in Appendix B, has the value

$$(-1)^{\nu} \frac{(\mu + |\nu|)!}{(\mu - |\nu|)!} (1 - x^2)^{-1} [P^{\nu}_{\mu}(x)]^{-2}.$$

Accordingly, eq. (90) becomes

$$I = (-1)^{\nu} \frac{(\mu + |\nu|)!}{(\mu - |\nu|)!} \int_1^{\infty} \frac{dx}{(x^2 - 1)[P_\mu^\nu(x)]^2} \int_1^x dy\, \phi_1(y) \int_1^x dz\, \phi_2(z). \tag{91}$$

Using eq. (91), the integral $Z^{\nu}_{\mu p q p' q'}$ assumes the final form

$$Z^{\nu}_{\mu p q p' q'} = I^{\nu}_{\mu q}(\zeta_1) I^{\nu}_{\mu q'}(\zeta_2) \int_1^{\infty} \frac{dx}{(x^2 - 1)} \left[\frac{(\mu - |\nu|)!}{(\mu + |\nu|)!\, P_\mu^\nu(x)}\right]^2 \times K^{\nu}_{\mu p}(x, \delta_1) K^{\nu}_{\mu p'}(x, \delta_2), \tag{92}$$

where $K^{\nu}_{\mu p}$ is given in eq. (38). Methods for evaluating $I^{\nu}_{\mu q}$ and $K^{\nu}_{\mu p}$ appear in Appendixes C and D, respectively.

Equation (92) is a relatively satisfactory form for $Z^{\nu}_{\mu p q p' q'}$ because, except for the one-dimensional integral over x, the two charge distributions have been completely separated in a way which produces well-characterized functions. The x integration is to be carried out numerically, and eq. (92) has the desirable feature that its integrand has no change of sign within the integration range, independently of the values of δ_1, δ_2, or the indices.

The choice and organization of the computational methods for evaluating the general two-center integral must be made with great care, because this evaluation procedure will be a rate-determining step in many molecular calculations. We first recognize that the important quantity is not the work of obtaining a single integral, but rather that of obtaining *all* the integrals which are needed in a given problem. Accordingly, we seek methods in which the same intermediate quantities can be used in as many integrals as possible. We note that eq. (92) has the feature that the functions $I^{\nu}_{\mu q}$ and $K^{\nu}_{\mu p}$ are determined by individual charge distributions, so that it should be possible to re-use these functions in all integrals with a common charge distribution for either electron, provided that the integral involves the same pair of centers. This advantage can be realized, however, only if the method for numerical quadrature of eq. (92) utilizes the same set of x values in different integrals. We therefore employ a single numerical integration scheme for the entire set of two-center integrals.

To determine a satisfactory numerical integration method we studied the behavior of $Z^{\nu}_{\mu p q p' q'}$, finding that the values of

δ_1 and δ_2 are the most significant quantities affecting the choice of an optimum integration scheme. After much investigation, we decided to base our choice of numerical quadrature formulae on the average of all the δ values appearing in a molecular calculation. We found it satisfactory to use moderate order formulae with the order and point spacing taken in ways which were dependent upon the average δ value. Equation (92) is of a form which can most readily be associated with Gauss–Laguerre quadrature (Rabinowitz and Weiss, 1959). However, we found such formulae to be less useful than Lobatto quadrature (Michels, 1963), which can be applied to the variable $1/x$, with integration limits 0 and 1. In setting up the work, use is made of the fact that the integrand is known to vanish at $x = 1$, and that at $x = \infty$ the $K^{\nu}_{\mu p}$ assume a simple form (Harris, 1960).

The next step in optimizing the actual numerical computations is to re-examine eqs. (85) and (92) to see how the total number of operations involved can be minimized. Noting that the numerical quadrature corresponds to replacing the integral by a weighted summation, eqs. (85) and (92) are essentially

$$X_{ab,cd} = 2\pi^2 R \sum_{\mu,\nu} (2\mu + 1) \frac{(\mu + |\nu|)!}{(\mu - |\nu|)!} \sum_{p,q} \sum_{p',q'} B^{ab}_{p,q,\nu} B^{cd}_{p',q',-\nu}$$
$$\times I^{\nu}_{\mu q}(\zeta_1) I^{\nu}_{\mu q'}(\zeta_2) \sum_j \frac{w_j}{(x_j^2 - 1)[P^{\nu}_{\mu}(x_j)]^2} K^{\nu}_{\mu p}(x_j, \delta_1) K^{\nu}_{\mu p'}(x_j, \delta_2). \quad (93)$$

The x_j and w_j are the integration points and weights, respectively. A nearly optimum rearrangement of eq. (93) is to the form

$$X_{ab,cd} = \sum_{\mu,\nu,j} G^{ab}_{\mu,\nu,j}(\delta_1, \zeta_1) G^{cd}_{\mu,-\nu,j}(\delta_2, \zeta_2), \quad (94)$$

where $G^{ab}_{\mu,\nu,j}(\delta, \zeta)$ depends upon a single charge distribution and is given by the formula

$$G^{ab}_{\mu,\nu,j}(\delta, \zeta) = \left[\frac{2\pi^2 R(2\mu + 1)(\mu + |\nu|)! w_j}{(x_j^2 - 1)(\mu - |\nu|)!}\right]^{1/2} \frac{1}{P^{\nu}_{\mu}(x_j)}$$
$$\times \sum_p \left[\sum_q B^{ab}_{p,q,\nu} I^{\nu}_{\mu q}(\zeta)\right] K^{\nu}_{\mu p}(x_j, \delta). \quad (95)$$

It is now clear that the computation of a set of integrals on a given pair of centers involves calculation of G arrays for all

relevant charge distributions, followed by pairwise merging of these arrays as specified by eq. (94).

Calculation of the G arrays given in eq. (95) is straightforward, but on present machines takes considerably longer than the time needed to transfer an already existent array from one storage medium to another. It therefore appears best to proceed by computing all the necessary G arrays, storing them where advisable, and reading them into the active storage of the computer as needed. Since all but the smallest problems involve more G arrays than can simultaneously be accommodated in the high-speed storage of a computer, it is important to arrange the work so as to minimize both the length of the G arrays and the number of times each array must be read into high-speed storage.

Two factors influence the length of the G arrays, namely, the presence of symmetry zeroes in the B coefficients and the convergence rate of the Neumann expansion, which determines the extent of the μ summation. For diatomic molecules, the use of axially oriented orbitals of definite symmetry restricts the $G_{\mu,\nu,j}$ to a single value of ν. The convergence of the Neumann expansion is mainly determined by the behaviour of the functions $I^{\nu}_{\mu q}$, so that an early step in construction of the G array can be an examination of the $I^{\nu}_{\mu q}$, leading to a decision as to the number of μ values to be retained. Suitable programming causes all array elements which have been eliminated to be treated as zeroes.

The most important step in reducing the number of array transfers is to assign high-speed storage so as to maximize the number of arrays which can be accommodated at one time. We have found it advisable to arrange the computations so that no other program or datum occupies high-speed storage while the array handling is in progress. As an illustration, let us suppose we can provide space for n arrays. If transfers from the auxiliary storage are adequately buffered, the best arrangement is to load in $n - 1$ arrays, to make all pairwise combinations of these, and then to read successively all the remaining arrays into the n-th array space, combining each new array with each of the original $n - 1$ arrays. Then the first $n - 1$ arrays are replaced with any other $n - 1$ arrays, and the process outlined above is repeated with the exception that the original $n - 1$ arrays need not be considered further, since all integrals involving them have already

been computed. Continuing in this way, we eliminate $n - 1$ arrays on each cycle until all pairwise combinations of G arrays have been formed. If transfer buffering is not complete, it may be most economical to use two or more array spaces in the role just outlined for the n-th array space, so that one array may be read while another is being processed. Further details of the array handling depend on the nature of the auxiliary storage. For example, if tape storage is used, it may be convenient to divide the arrays among two tapes so as to allow time for repositioning of one tape while the other is being read.

D. One-center Expansions for Multi-center Integrals

The general plan for evaluating multi-center integrals through use of single-center expansions is to obtain the two charge distributions as spherical harmonic expansions about a common center, after which transformations similar to those discussed for the two-center integrals can be carried out. Let us suppose that the expansions are to be made with respect to the space-fixed molecular axial system introduced in Section II-A, and that they are of the form

$$\Psi_a^*(\mathbf{r}_1)\Psi_b(\mathbf{r}_1) = \sum_{l,m} f_{l,m}^{ab}(r_1) P_l^m(\cos\theta_1)\, e^{im\phi_1} \tag{96}$$

and

$$\Psi_c^*(\mathbf{r}_2)\Psi_d(\mathbf{r}_2) = \sum_{l,m} f_{l,m}^{cd}(r_2) P_l^m(\cos\theta_2)\, e^{im\phi_2}, \tag{97}$$

where $f_{l,m}^{ab}$ and $f_{l,m}^{cd}$ are obtained by methods to be discussed. We also use the Green's function expansion, eq. (14), for $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$. When the angular integrations are performed and the orthogonality properties of the spherical harmonics are invoked, the general multi-center electron repulsion integral reduces to the form

$$X_{ab,cd} = \sum_{\mu,\nu} \left(\frac{4\pi}{2\mu+1}\right)^2 \frac{(\mu+|\nu|)!}{(\mu-|\nu|)!} \int_0^\infty r_1^2\, dr_1 \times \int_0^\infty r_2^2\, dr_2 f_{\mu,\nu}^{ab}(r_1) f_{\mu,-\nu}^{cd}(r_2) \frac{r_-^\mu}{r_+^{\mu+1}}. \tag{98}$$

Equation (98) is now subjected to an integral transformation (Harris and Michels, 1965a, 1966), leading to

$$X_{ab,cd} = \sum_{\mu,\nu} \frac{16\pi^2(\mu + |\nu|)!}{(2\mu + 1)(\mu - |\nu|)!} \int_0^\infty \frac{dx}{x^{2\mu+2}} \times \int_0^x dr_1\, r_1^{\mu+2} f^{ab}_{\mu,\nu}(r_1) \int_0^x dr_2\, r_2^{\mu+2} f^{cd}_{\mu,\nu}(r_2). \quad (99)$$

The transformation is proved by a process similar to that described in Section V-C. However, in place of eq. (88) we start with

$$I = \int_0^\infty dx\, x^{-2\mu-1} \left[x^{\mu+2} f^{ab}_{\mu,\nu}(x) \int_0^x dr_2\, r_2^{\mu+2} f^{cd}_{\mu,-\nu}(r_2) + x^{\mu+2} f^{cd}_{\mu,-\nu}(x) \int_0^x dr_1\, r_1{}^{\mu+2} f^{ab}_{\mu,\nu}(r_1) \right]. \quad (100)$$

All the integrations appearing in eq. (99) are to be evaluated numerically, so the x integration may be regarded as a sum over points x_j with weights w_j. The computational form equivalent to eq. (99) is therefore

$$X_{ab,cd} = \sum_{\mu,\nu,j} G^{ab}_{\mu,\nu,j} G^{cd}_{\mu,-\nu,j} \quad (101)$$

with

$$G^{ab}_{\mu,\nu,j} = \frac{4\pi}{x_j^{\mu+1}} \left[\frac{w_j(\mu + |\nu|)!}{(2\mu + 1)(\mu - |\nu|)!} \right]^{1/2} \int_0^{x_j} r^{\mu+2} f^{ab}_{\mu,\nu}(r)\, dr. \quad (102)$$

The integral in eq. (102) is also evaluated as a weighted sum, and it is clearly most efficient to compute ${}_0\int^{x_j}$ as the sum of ${}_0\int^{x_{j-1}}$ and ${}_{x_{j-1}}\int^{x_j}$, *i.e.* to employ point-to-point integration formulae. It is found that the final result $X_{ab,cd}$ is far more sensitive to the method of quadrature used for eq. (102) than to the method used for the x integration of eq. (99). The sensitivity arises from the fact that the integrand in eq. (102) may change sign at r values determined by the geometry and the quantum numbers of the orbital involved. The integrand also has slope and higher-order singularities at the r value corresponding to the orbital center but, as we have noted in earlier work (Harris and Michels, 1966), these singularities do not create significant numerical problems. The behavior of the integrand in eq. (102) suggests that point-to-point integration formulae would be preferable to higher-order formulae for this integration. On the other hand, higher-order formulae do prove useful for the x integration, as

the difficulties encountered in the r integrals are no longer significant owing to the smoothing process associated with the prior integration over r.

After study of many integration methods, we found that the x integration could be done satisfactorily by transforming the integration interval to $(-1, 1)$ and using a 34-point Lobatto formula (Michels, 1963). Lobatto quadrature is especially suitable in this application because the end points of the integration range are special cases of the integrand and can be easily evaluated. When the points selected for the x integral were used, the r integrals were evaluated with the aid of a quadratic interpolating formula based on a 4-point interval, the middle two points of which are the end points of the incremental integral $\int_{x_{j-1}}^{x_j}$. The procedure we used causes the approximations in adjacent segments of the r integration to join smoothly in slope. For details, see Harris and Michels (1966).

Equation (101) is of a form similar to that of eq. (94), and leads to similar computational problems. We note that because the same coordinate system is used for the expansion of all charge distributions, all the electron-repulsion integrals can be generated from a single complete set of G arrays.

It is possible to use some features of the foregoing discussion to produce formulations for overlap and nuclear attraction integrals. However, we do not use these formulations, because they are less accurate than the methods we have already described for these integrals. Nevertheless, the one-center methods for the overlap and nuclear attraction integrals can be of interest, particularly for checking numerical results. The overlap integral S_{ab} is, as may be seen from eq. (96), given by

$$S_{ab} = 4\pi \int_0^\infty f_{0,0}^{ab}(r) r^2 \, dr, \tag{103}$$

and this is the integral appearing in eq. (102) for $x_j \to \infty$ and $\mu = \nu = 0$.

The nuclear attraction integral $V_{ab,c}$ may be formed from eq. (96) and the Green's function expansion for $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$,

$$V_{ab,c} = \sum_{\mu,\nu} \left(\frac{4\pi}{2\mu + 1} \right) P_\mu^\nu(\cos \Theta_c) \, e^{i\nu\Phi_c} \int_0^\infty r^2 f_{\mu,\nu}^{ab}(r) \frac{r_-^l}{r_+^{l+1}} \, dr \tag{104}$$

with r_+ and r_- the greater and lesser of r and R_C. Equation (104) may be used as given, or it may be converted into an expression similar in form to eq. (99), namely:

$$V_{ab,c} = \sum_{\mu,\nu} 4\pi P_\mu^\nu(\cos\Theta_c)\, e^{i\nu\Phi_c} R_c^\mu \int_{R_c}^{\infty} \frac{dx}{x^{2\mu+2}} \int_0^x dr\, r^{\mu+2} f_{\mu,\nu}^{ab}(r). \quad (105)$$

The validity of eq. (105) becomes apparent if we recognize that eq. (104) can be thought of as a case of eq. (98) with $f_{\mu,-\nu}^{cd}(r_2)$ taken as

$$\frac{(2\mu+1)}{4\pi} \frac{(\mu - |\nu|)!}{(\mu + |\nu|)!} r_2^{-2} P_\mu^\nu(\cos\Theta_c)\, e^{i\nu\Phi_c} \delta(r_2 - R_C),$$

where δ stands for a one-dimensional Dirac delta function. The difficulty with eq. (104) or (105) lies in the convergence of the series, which is much slower than for most electron-repulsion integrals.

We next examine the methods by which we may evaluate the expansion coefficients $f_{l,m}^{ab}$. In general, the plan is to expand Ψ_a^* and Ψ_b individually about a common expansion point, which we call **P**, after which we multiply the expansions together. The exact manner of doing this depends upon the fact that our formulae for expanding an orbital about a new origin require that the new origin be located on the positive polar axis of the old coordinate system. It is also pertinent to note that different possible ways of handling the expansions vary in their computation times.

Our method for obtaining the $f_{l,m}^{ab}$ consists of the following steps:

(1) The coordinate axes used to describe Ψ_a^* are rotated so that the expansion point **P** lies on the positive polar axis of the new coordinate system for Ψ_a^*. This results in Ψ_a^* being described by a linear combination of orbitals, all with quantum numbers n_a and l_a, but with a range of m values.

(2) Orbital Ψ_a^* is next expanded about **P**. This step results in coefficients which are functions of the radial distance r, multiplied by spherical harmonics in an axial system parallel to that newly obtained in step (1) for Ψ_a^*. The coefficients will have a range of l and m values, and, owing to their complicated r-dependence, are obtained numerically for the particular values of r which will later be needed in the numerical integrations.

(3) The axes used for Ψ'_b are rotated so their positive polar axis points toward **P**.

(4) Orbital Ψ'_b is expanded about **P**, in spherical harmonics in an axial system parallel to that obtained in step (3).

(5) The expansion of Ψ^*_a about **P** is transformed so that its spherical harmonics are given in the coordinate system used for Ψ'_b in step (4).

(6) The expansions for Ψ^*_a and Ψ'_b, which are now in the same axial system, are combined into a single expansion. The coefficients are listed numerically for the r values used in steps (2) and (4), and the spherical harmonics are still in the coordinate system used in step (4).

(7) The expansion of $\Psi^*_a\Psi'_b$ obtained in step (6) is transformed so that its spherical harmonics are given in the space-fixed axial system to be used for all charge distributions.

The rotational transformations needed for steps (1), (3), (5), and (7) are carried out by using eq. (6). To determine the Eulerian angles of the transformation of step (1), we note that the axial orientation after that step has been carried out is directed along a ray opposite to that defined by the polar coordinates Θ_a, Φ_a, *i.e.* a ray directed in the direction defined by $\pi - \Theta_a$, $\pi + \Phi_a$. The latter ray is specified by Eulerian angles $(\pi + \Phi_a, \pi - \Theta_a, 0)$, so that the rotation to be carried out in step (1) is from Eulerian angles $(\alpha_a, \beta_a, \gamma_a)$ to $(\pi + \Phi_a, \pi - \Theta_a, 0)$. Corresponding arguments indicate that the rotation carried out in step (3) is from $(\alpha_b, \beta_b, \gamma_b)$ to $(\pi + \Phi_b, \pi - \Theta_b, 0)$. It is then clear that the rotation involved in step (5) is from $(\pi + \Phi_a, \pi - \Theta_a, 0)$ to $(\pi + \Phi_b, \pi - \Theta_b, 0)$, and that the rotation of step (7) is from $(\pi + \Phi_b, \pi - \Theta_b, 0)$ to the reference orientation (0, 0, 0).

By using the CALL ROT procedure described previously, the Eulerian angles for the transformations discussed above may be more explicitly specified as follows:

For step (1), as $(\bar{\alpha}_a, \bar{\beta}_a, \bar{\gamma}_a)$, given by

$$\text{CALL ROT } (\alpha_a, \beta_a, \gamma_a, \pi + \Phi_a, \pi - \Theta_a, 0, \bar{\alpha}_a, \bar{\beta}_a, \bar{\gamma}_a)$$

For step (3), as $(\bar{\alpha}_b, \bar{\beta}_b, \bar{\gamma}_b)$, given by

$$\text{CALL ROT } (\alpha_b, \beta_b, \gamma_b, \pi + \Phi_b, \pi - \Theta_b, 0, \bar{\alpha}_b, \bar{\beta}_b, \bar{\gamma}_b)$$

For step (5), as $(\alpha_{ab}, \beta_{ab}, \gamma_{ab})$, given by

CALL ROT $(\pi + \Phi_a, \pi - \Theta_a, 0, \pi + \Phi_b, \pi - \Theta_b, 0, \alpha_{ab}, \beta_{ab}, \gamma_{ab})$

For step (7), as $(\pi, \pi - \Theta_b, -\Phi_b)$.

The translational transformation needed for steps (2) and (4) has been found to be of the form

$$r_a^{n_a-1} \, e^{-\delta_a r_a} P_{l_a}^{m_a}(\cos \theta_a) \, e^{im\phi_a}$$

$$= \delta_a^{-n_a+1} \sum_{j=|m_a|}^{\infty} V_{n_a,l_a,j}^{m_a}(\delta_a r, \, \delta_a R) P_j^{m_a}(\cos \bar{\theta}_a) \, e^{im_a\bar{\phi}_a} \quad (106)$$

where (r_a, θ_a, ϕ_a) and $(r, \bar{\theta}_a, \bar{\phi}_a)$ denote parallel polar coordinate systems centered at **A** and **P**, respectively, with **P** situated on the positive polar axis of the **A** system, with $R = |\mathbf{P} - \mathbf{A}|$. The coefficients $V_{n,l,j}^{m}$ are determined recursively for each needed value of r, by methods developed by the authors (Harris and Michels, 1965a, b). These methods are reviewed in Appendix F.

When eqs. (6) and (106) are applied to a real orbital Ψ_a at arbitrary orientation, we have, after steps (1) and (2):

$$\Psi_a = \delta_a^{-n_a+1} \sum_{\sigma=-l_a}^{l_a} \sum_{j=|\sigma|}^{\infty} W_{ja}^{\sigma}(r) P_j^{\sigma}(\cos \bar{\theta}_a) \, e^{i\sigma\bar{\phi}_a}, \quad (107)$$

with

$$W_{j_a}^{\sigma}(r) = \frac{1}{2}[D_{l_a}^{m_a,\sigma}(\bar{\alpha}_a, \bar{\beta}_a, \bar{\gamma}_a) + D_{l_a}^{-m_a,\sigma}(\bar{\alpha}_a, \bar{\beta}_a, \bar{\gamma}_a)] V_{n_a,l_a,j}^{\sigma}(\delta_a r, \, \delta_a R), \quad m_a \geqslant 0 \quad (108a)$$

and

$$W_{ja}^{\sigma}(r) = \frac{i}{2}[D_{l_a}^{m_a,\sigma}(\bar{\alpha}_a, \bar{\beta}_a, \bar{\gamma}_a) - D_{l_a}^{-m_a,\sigma}(\bar{\alpha}_a, \bar{\beta}_a, \bar{\gamma}_a)] V_{n_a,l_a,j}^{\sigma}(\delta_a r, \, \delta_a R), \quad m_a < 0. \quad (108b)$$

The arguments of the rotation coefficients $D_l^{m,\sigma}$ are those discussed previously. An analysis similar to eqs. (107) and (108) gives the expansion of Ψ_b after steps (3) and (4).

The rotational transformation of step (5) causes Ψ_a to be given, not by eq. (107), but by

$$\Psi_a = \delta_a^{-n_a+1} \sum_{=0}^{\infty} \sum_{\sigma=-j}^{j} W_{ja,b}^{\sigma}(r) P_j^{\sigma}(\cos \bar{\theta}_b) \, e^{i\sigma\bar{\phi}_b}. \quad (109)$$

Note that the angular coordinates are now in the system related to the direction of the point **B**. On using eqs. (6) and (107), it is seen that $W^{\sigma}_{ja,b}$ in eq. (109) satisfies

$$W^{\sigma}_{ja,b}(r) = \sum_{\tau=-j}^{j} D^{\tau,\sigma}_{j}(\alpha_{ab}, \beta_{ab}, \gamma_{ab}) W^{\tau}_{ja}(r). \tag{110}$$

We now have expansions of both Ψ^*_a and Ψ_b in the same coordinate system, and we are ready to proceed to step (6). Mutiplying eq. (110) and the equation corresponding to eq. (107) for Ψ_b, we reduce the products of spherical harmonics with the Clebsch–Gordan formula, eq. (54). The result is an expansion of the form

$$\Psi^*_a \Psi_b = \sum_{\mu,\nu} f^{\nu}_{\mu b}(r) P^{\nu}_{\mu}(\cos \bar{\theta}_b)\, e^{i\nu\bar{\phi}_b}, \tag{111}$$

with

$$f^{\nu}_{\mu b}(r) = \delta_a^{-n_a+1} \delta_b^{-n_b+1} \sum_{j=0}^{\infty} \sum_{k} \sum_{\sigma} C^{\sigma,\nu+\sigma}_{\mu,j,k} W^{-\sigma}_{ja,b}(r) W^{\nu+\sigma}_{kb}(r). \tag{112}$$

Finally, the rotation of step (7) leads to the expansion given in eq. (96), so that the $f^{ab}_{\mu,\nu}$ satisfy

$$f^{ab}_{\mu,\nu}(r) = \sum_{\sigma} D^{\sigma,\nu}_{\mu}(\pi, \pi - \Theta_b, -\Phi_b) f^{\sigma}_{\mu b}(r). \tag{113}$$

An examination of the steps involved in calculating $X_{ab,cd}$ reveals that (i) each orbital must be expanded about the expansion center, (ii) each pair of orbitals must be combined to form a charge distribution, and (iii) pairs of charge distributions must be multiplied together to form integrals. For small and moderate-sized problems the formation of charge distributions is the most time-consuming part of the overall process, while only for large systems does the pairwise merging of charge distributions become the rate-determining step in the calculations. This fact indicates the importance of optimizing the process of expanding each charge distribution.

VI. COMPUTATIONAL DETAILS AND RESULTS

The analysis presented in this report has been tested through the development of digital computer programs for all the basic

molecular integrals which we have described. We give in this Section some typical results, together with a discussion of computation time and accuracy.

The one-electron, one- and two-center integrals described in Section III include the overlap integral, the kinetic energy integral, and one- and two-center nuclear attraction integrals. As described there, these integrals can all be evaluated in terms of the well-known A and B functions which can be computed to the limit of the machine accuracy by the methods described in Appendix C. Thus, using IBM 7094 equipment we are able to compute all these integrals to seven significant figures and have verified this accuracy for all such integrals with quantum numbers $n \leqslant 7, l \leqslant 3, |m| \leqslant l$. Separate computation times for these integrals are not known since these integrals are most efficiently evaluated in a unified program. However, for the set of these integrals arising from a single charge distribution, a typical evaluation time is well below 100 msec.

Next to be considered are the three-center nuclear attraction integrals. We give in Table 1 values for several such integrals which were computed by the methods outlined in Section IV. For comparison, we also give values obtained by the previously reported one-center expansion method (Barnett, 1963), and we indicate the length of the series expansions required in each method for accuracy to five significant figures. The integrals evaluated by using the one-center expansion method are, however, not always accurate to this number of figures, owing to errors arising from the numerical integration procedures. It is seen from Table 1 that for certain integrals, single-center expansion methods require a great number of terms for even four-figure accuracy, in contrast to the rapid convergence indicated for our method of analysis. For most of the three-center nuclear attraction integrals that we have examined by our method, a higher accuracy of six to seven significant figures is obtainable with the addition of only a few more terms in the series expansion. We have therefore adjusted our programs to give a minimum of six significant figures for these integrals. This can be readily accomplished by examining the magnitudes of the $I^{\nu}_{\mu q}$ integrals given by eq. (36), since these integrals control the rate of convergence of the infinite series expansion given in eq. (33). The time required to evaluate a

typical three-center nuclear attraction integral by our method is of the order of 300 msec on IBM 7094 equipment.

The rate-determining step in any molecular calculation is the time required for computation of the electron-repulsion integrals. In Section V we described four different computationally useful methods for evaluating these integrals. One-center electron-repulsion integrals are best evaluated by use of eq. (51). Note

TABLE 1. Three-center Nuclear Attraction Integrals

	One-center expansion[a]		Ellipsoidal expansion[b]	
	Integral value	No. of terms in expansion	Integral value	No. of terms in expansion
Benzene				
$(2s_{C_1}1s_{C_2}\|r_{C_4}^{-1})$	0.0069952	>29	0.0070016	5
$(2p\sigma_{C_1}2s_{C_2}\|r_{C_4}^{-1})$	0.012183	>29	0.012174	5
$(1s_{C_2}2s_{C_4}\|r_{C_4}^{-1})$	0.00082161	17	0.00082133	7
Methane				
$(1s_H1s_{H'}\|r_C^{-1})$	0.16765	15	0.16765	2
$(1s_H2p\sigma_{H'}\|r_C^{-1})$	0.010721	20	0.010728	5
Ethane[c]				
$(1s_H1s_{C'}\|r_C^{-1})$	0.0035493	29	0.0035491	10
$(2p_{y_C}2p_{y_{C'}}\|r_H^{-1})$	0.059781	15	0.059781	4

[a] Pitzer *et al.*, 1963.
[b] This work.
[c] R(C–H) = 2.0825 Bohr; R(C′–H) = 4.1095 Bohr.

that the single-center expansion coefficients $F_{l,m}^{ab}$ need be made only once for each charge distribution but can be used repeatedly for each integral in which the charge distribution appears. This procedure results in a substantial saving in computation time when evaluating a group of one-center electron-repulsion integrals. We find average times of 25 msec for such integrals with an indicated accuracy at the machine limit of seven significant figures.

The two-center integrals of Coulomb-type are best evaluated by the use of the convolution method described in Section V-B. A little thought will show that the expansion coefficients $F^{ab}_{l,m}$ are, except for a rotational transformation, identical with those needed for evaluating the one-center electron-repulsion integrals. We have therefore arranged our computations to permit evaluation of both types of integrals in a unified program. The time required to evaluate a single Coulomb integral depends mainly on the screening parameters for the two charge distributions. For equal δ, an average time is 10 msec. For unequal δ such that δ_1/δ_2 is near unity, the most time-consuming case, the evaluation time increases to about 40 msec. Our methods indicate an accuracy of six to seven significant figures for all the quantum numbers and screening constant ratios that we have examined.

For two-center integrals other than of Coulomb type, we employ the ellipsoidal expansion method discussed in Section V-C. The computational details of this method have been described before (Harris, 1960) and the only significant change has been the generalization to higher quantum numbers and the use of more accurate quadrature techniques for the single numerical integration that is required. The average time required to evaluate a two-center integral by this method is strongly dependent upon the number of such integrals which occur in a molecular calculation. This is because the functions $G^{ab}_{\mu,\nu,j}$ given in eq. (95) depend upon a single charge distribution and can therefore be used repeatedly for a group of electron-repulsion integrals. The indicated summation shown in eq. (94) requires an average of only 5 msec, so the actual time is controlled by the speed of transfer of the many G tables into and out of the high-speed storage. We have been able to show average times of about 16 msec per integral for large molecular problems. Our indicated accuracy is six to seven significant figures and is primarily a function of the accuracy of the numerical integration.

The most difficult and certainly the most time-consuming integrals are the multi-center electron-repulsion integrals which we evaluate by the general expansion technique given in Section V-D. In our general method of analysis for these integrals there are three steps which must be separately examined.

The first step is the transformation of an orbital from its

particular coordinate system to the single reference system of the molecule, as shown in eq. (107). This step must be performed n times in an n-orbital problem. We find that this orbital transformation requires a maximum of 40 msec, the time depending somewhat upon the quantum numbers of the orbital. This step turns out never to be rate-controlling.

The second step involves the pairwise combination of the transformed orbitals to form charge distributions as shown in eqs. (111) and (112). This operation must be performed $n(n + 1)/2$ times in an n-orbital problem and is the rate-determining step for small molecules. We find average computation times of five to six seconds per charge distribution with our present equipment. This time would be reduced substantially if the many Clebsch–Gordan coefficients which are needed could be produced or read into high-speed memory more efficiently. The numerical integration shown in eq. (102) requires a negligible amount of time.

The final step in evaluating a general multi-center electron-repulsion integral involves the pairwise merging of all charge distributions as indicated in eq. (101). This operation must be performed $n(n + 1)(n^2 + n + 2)/8$ times in an n-orbital problem and becomes rate-controlling for large molecules. An average time to perform the operation indicated in eq. (101) is 200 msec, including the time required to read the charge distributions off disk tracks. Thus the time required to evaluate a single general multi-center integral ranges from about 12 sec, if only one integral is required, to about 200 msec if several thousand are required. An average time of 300 msec has been achieved for the methane molecule. [But see addendum on p. 266.]

The accuracy of our evaluations is controlled primarily by the numerical quadrature techniques that we employ. The number of terms retained in the expansions of the orbitals is optimized separately for each orbital and therefore, except when the expansion length is limited by machine capacity, it influences computing speed, but not accuracy. We give in Table 2 some typical results for the methane and benzene molecules. For comparison we give the integral values reported by Shavitt (1963) and those calculated by using the programs of Pitzer *et al.* (1963). Our indicated accuracy is between four and five significant figures for most of the integrals which we have examined.

It is obvious from the above discussion that, for a polyatomic molecule, the evaluation of the multi-center electron-repulsion integrals is still the rate-controlling factor in a molecular-energy calculation. All one-electron and two-electron, two-center integrals can be evaluated at speeds which are about an order of magnitude

TABLE 2. Three- and Four-center Integrals

Integral	Method of Shavitt[a]	Method of Barnett[b]	This work
Benzene[c]			
(12|13)	0.004112		0.004111
(12|45)	0.01374		0.01377
(13|24)	0.000578		0.0005780
(13|46)	0.000437		0.0004370
Methane[d]			
(12|34)	0.03068	0.03068	0.03068
(12|13)	0.03569	0.03570	0.03570
$(p_1p_2\|p_3p_4)$			0.03849
$(p_1p_2\|p_1p_3)$			0.04265

[a] Shavitt, 1963.
[b] Pitzer *et al.*, 1963.
[c] Integrals involving π orbitals on C atoms as numbered.
[d] First two integrals are for $1s$ orbitals on H atoms as numbered; second two integrals are for $2p\sigma$ orbitals on H atoms as numbered, with $+z$ orientation for each orbital toward the C atom, and with $\delta_{2p}/\delta_{1s} = 5/3$.

faster than those achieved for the three- and four-center integrals. However, the unified computational approach which we have outlined now permits single energy calculations for small polyatomic molecules such as methane in a few minutes of overall computation time. Such times will be reduced still further by the use of the new generation of computers such as the Univac 1108 or the CDC 6600. We believe that methods such as those outlined here will make practical the use of Slater-type orbitals for studies of the electronic structures of polyatomic molecules *ab initio*.

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APPENDIX A

Rotational Coordinate Transformations

We specify a rotation by an axial ray and by a rotation angle. The angle is to be measured in a counter-clockwise sense when looking toward the origin from a point in the positive direction along the ray. The coordinate systems we use are right-handed, by which we mean that a rotation by an angle $\pi/2$ about the z-axis carries the positive x-axis (the $\phi = 0$ half-plane) into the position originally occupied by the positive y-axis (the $\phi = \pi/2$ half-plane). The Eulerian angles (α, β, γ) then refer to the followed ordered operations on a set of coordinate axes: (1) Rotation by an angle α about the z-axis; (2) rotation by an angle β, $0 \leqslant \beta \leqslant \pi$, about the new y-axis; (3) rotation by an angle γ about the new z-axis.

In the main text we repeatedly require the rotational transformation (α, β, γ) which converts axes from orientation $(\alpha_1, \beta_1, \gamma_1)$ to orientation $(\alpha_2, \beta_2, \gamma_2)$. We represent this relation symbolically by

$$(\alpha, \beta, \gamma)(\alpha_1, \beta_1, \gamma_1) = (\alpha_2, \beta_2, \gamma_2) \tag{114}$$

and we designate the calculation of (α, β, γ) by the procedure CALL ROT $(\alpha_1, \beta_1, \gamma_1, \alpha_2, \beta_2, \gamma_2, \alpha, \beta, \gamma)$. The specific equations relating these variables are the following:

$$\cos\beta = \cos\beta_1 \cos\beta_2 + \sin\beta_1 \sin\beta_2 \cos(\alpha_2 - \alpha_1) \tag{115}$$

$$\alpha = -\gamma_1 + \theta \tag{116}$$

$$\gamma = \gamma_2 - \chi \tag{117}$$

with

$$\sin\theta = \frac{\sin\beta_2 \sin(\alpha_2 - \alpha_1)}{\sin\beta} \tag{118a}$$

$$\cos\theta = \frac{-\sin\beta_1 \cos\beta_2 + \cos\beta_1 \sin\beta_2 \cos(\alpha_2 - \alpha_1)}{\sin\beta} \tag{118b}$$

$$\sin\chi = \frac{\sin\beta_1 \sin(\alpha_2 - \alpha_1)}{\sin\beta} \tag{119a}$$

$$\cos\chi = \frac{\cos\beta_1 \sin\beta_2 - \sin\beta_1 \cos\beta_2 \cos(\alpha_2 - \alpha_1)}{\sin\beta} \tag{119b}$$

If $\sin\beta = 0$, eqs. (116)–(119) become ill-defined, and we use instead

$$\alpha = (\alpha_2 - \alpha_1)(\text{sign of } \cos\beta_1) \tag{120}$$

$$\gamma = \gamma_2 - \gamma_1 \cos\beta. \tag{121}$$

The coefficients needed to describe an axial rotation are related to the Eulerian angles by the formulae of eqs. (7)–(9). However, as indicated in the main text, the explicit formula is inconvenient for actual computation of the quantities $\mathrm{d}^l(\cos\beta)_{m,\sigma}$. Letting t stand for $\cos\beta$, we calculate these coefficients for positive m and σ by the recurrence formulae given below. Application of the same formulae for $-t$, and the use of eq. (9), yields the $d^l_{m,\sigma}$ for all combinations of index signs. We start with

$$d^0_{0,0} = 1. \tag{122}$$

Then, for all needed l values, we use

$$d^l_{l,0} = -(2l-1)(1-t^2)^{1/2} d^{l-1}_{l-1,0}. \tag{123}$$

Next, for values of σ through $\sigma = m - 1$, we use

$$d^m_{m,\sigma} = -\left(\frac{1+t}{1-t}\right)^{1/2} \left(\frac{1}{m+\sigma}\right) d^m_{m,\sigma-1}. \tag{124}$$

Starting again from $d^0_{0,0}$, we proceed to all needed l values with

$$d^l_{0,l} = \frac{(1-t^2)^{1/2}}{2l} d^{l-1}_{0,l-1}. \tag{125}$$

Then we raise m stepwise to $m = \sigma$:

$$d^\sigma_{m,\sigma} = (\sigma - m + 1)\left(\frac{1+t}{1-t}\right)^{1/2} d^\sigma_{m-1,\sigma}. \tag{126}$$

Finally, we produce the general coefficient $d^l_{m,\sigma}$ by increasing l in steps from $d^m_{m,\sigma}$, if $m \geqslant \sigma$, or from $d^\sigma_{m,\sigma}$, if $\sigma > m$. In either case, the formula we use is

$$\frac{(l+\sigma+1)(l-m+1)}{l+1} d^{l+1}_{m,\sigma} = (2l+1)\left[t - \frac{m\sigma}{l(l+1)}\right] d^l_{m,\sigma} - \frac{(l-\sigma)(l+m)}{l} d^{l-1}_{m,\sigma}. \tag{127}$$

When applying eq. (127) for the first step, for which $l = \max(m, \sigma)$, we may set $d^{m-1}_{m,\sigma}$ or $d^{\sigma-1}_{m,\sigma}$ equal to zero.

APPENDIX B

Legendre Functions

The Legendre functions we use are defined, for the region $|x| \leqslant 1$, as follows:

$$P^m_l(x) = \frac{(-1)^m(1-x^2)^{|m|/2}}{2^l l!}\left(\frac{d}{dx}\right)^{l+|m|}(x^2-1)^l. \tag{128}$$

These functions satisfy the orthogonality relation

$$\int_{-1}^{1} P^m_l(x) P^m_{l'}(x)\, dx = \delta_{ll'}\left(\frac{2}{2l+1}\right)\frac{(l+|m|)!}{(l-|m|)!}, \tag{129}$$

the recurrence relations

$$(l-|m|+1)P^m_{l+1}(x) - (2l+1)xP^m_l(x) + (l+|m|)P^m_{l-1}(x) = 0, \tag{130}$$

$$(2l+1)(1-x^2)^{1/2}P^m_l(x) = P^{|m|+1}_{l-1}(x) - P^{|m|+1}_{l+1}(x), \tag{131}$$

$$(2l+1)(1-x^2)^{1/2}P_l^m(x) = (l-|m|+2)(l-|m|+1)P_{l+1}^{|m|-1}(x) - (l+|m|)(l+|m|-1)P_{l-1}^{|m|-1}(x), \quad (132)$$

and the formula (for $m > 0$)

$$\frac{d}{dx}[(1-x^2)^{m/2}P_l^m(x)] = (l+m)(l-m+1)(1-x^2)^{(m-1)/2}P^{m-1}(x). \quad (133)$$

The $P_l^m(x)$ are calculated from $P_0^0(x) = 1$ by upward recursion in l and m by using eqs. (130) and (132).

For $x > 1$, we require Legendre functions of both the first and the second kinds, with definitions

$$P_l^m(x) = \frac{(x^2-1)^{|m|/2}}{2^l l!}\left(\frac{d}{dx}\right)^{l+|m|}(x^2-1)^l, \quad (134)$$

$$Q_l^m(x) = (x^2-1)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|}Q_l(x), \quad (135)$$

$$Q_l(x) = \tfrac{1}{2}P_l(x)\ln\left(\frac{x+1}{x-1}\right) - \sum_{j=1}^{\leq \frac{1}{2}(l+1)}\frac{(2l-4j+3)}{(2j-1)(l-j+1)}P_{l-2j+1}(x). \quad (136)$$

With the above definitions, the Wronskian of P_l^m and Q_l^m is

$$P_l^m(x)\frac{dQ_l^m(x)}{dx} - Q_l^m(x)\frac{dP_l^m(x)}{dx} = \frac{(-1)^m(l+|m|)!}{(1-x^2)(l-|m|)!}. \quad (137)$$

In some of our work it is convenient to introduce modified Legendre functions $\mathscr{P}_l^m(x)$ and $\mathscr{Q}_l^m(x)$ for the region $x > 1$, defined as

$$\mathscr{P}_l^m(x) = \frac{(l-|m|)!}{(l+|m|)!}(x^2-1)^{|m|/2}P_l^m(x), \quad (138)$$

and

$$\mathscr{Q}_l^m(x) = \frac{(l-|m|)!}{(l+|m|)!}(x^2-1)^{|m|/2}Q_l^m(x). \quad (139)$$

In terms of these functions, the relations for $x > 1$ corresponding to eqs. (130)–(133) are

$$(l + |m| + 1)\mathscr{P}_{l+1}^{m}(x) - (2l + 1)\mathscr{P}_{l}^{m}(x) + (l - |m|)\mathscr{P}_{l-1}^{m}(x) = 0. \quad (140)$$

$$(2l + 1)(x^2 - 1)(\mathscr{P}_{l}^{m}(x) = (l - |m|)(l - |m| - 1)\mathscr{P}_{l-1}^{|m|+1}(x) - (l + |m| + 1)(l + |m| + 2)\mathscr{P}_{l+1}^{|m|+1}(x), \quad (141)$$

$$(2l + 1)\mathscr{P}_{l}^{m}(x) = \mathscr{P}_{l+1}^{|m|-1}(x) - \mathscr{P}_{l-1}^{|m|-1}(x), \quad (142)$$

and

$$\frac{\mathrm{d}}{dx}\mathscr{P}_{l}^{m}(x) = \mathscr{P}_{l}^{m-1}(x), \qquad m > 0, \quad (143)$$

Equations (140)–(143) are also satisfied by $\mathscr{Q}_{l}^{m}(x)$.

We calculate $\mathscr{P}_{l}^{m}(x)$ from $\mathscr{P}_{0}^{0}(x) = 1$ by upward recursion in l and m using eqs. (140) and (142). However, a similar process is unsatisfactory for $\mathscr{Q}_{l}^{m}(x)$ owing to the loss of significant figures at each recursive step. Instead, we employ downward recursion in l. When ratios

$$r_{l}^{m}(x) = \mathscr{Q}_{l+1}^{m}(x)/\mathscr{Q}_{l}^{m}(x) \quad (144)$$

are taken, the recurrence relation, eq. (140), becomes

$$r_{l-1}^{m}(x) = \frac{l - |m|}{(2l + 1)x - (l + |m| + 1)r_{l}^{m}(x)}. \quad (145)$$

The use of eq. (145) requires a knowledge of the asymptotic value of $r_{l}^{m}(x)$ for large l. Since the Legendre functions can be written in terms of the confluent hypergeometric function, we can readily find the asymptotic form to be

$$r_{l}^{m}(x) \approx \left(\frac{l - |m| + 1}{l + \frac{3}{2}}\right)[x - (x^2 - 1)^{1/2}]. \quad (146)$$

Starting from $r_{L}^{m}(x)$ as given by eq. (146), for some large L, we proceed downward with increasing accuracy at each step to $r_{|m|}^{m}(x)$. By choosing L sufficiently large we can obtain any

desired accuracy in the set of $r_l^m(x)$. We then start upward recursion using eq. (144) and the starting value

$$\mathscr{Q}_{|m|}^m(x) = \frac{(-1)^m}{(2|m|+1)!!}\left(\frac{1}{x - r_{|m|}^m(x)}\right). \tag{147}$$

Here $m!!$ stands for $m(m-2)(m-4)\ldots(2 \text{ or } 1)$.

For special cases of the nuclear attraction integral we require values of $\mathscr{Q}_l^m(x)$ for $x = 1$ (and, of course, for non-zero m). These values need not be computed by the methods already outlined but instead may be obtained from the simpler formula

$$\mathscr{Q}_l^m(1) = (-1)^m(2|m| - 2)!!\,\frac{(l-|m|)!}{(l+|m|)!}. \tag{148}$$

We also require Clebsch–Gordan coefficients as used in eq. (54) of the main text. When applied to the Legendre functions as defined in eq. (128), these coefficients satisfy

$$C_{\mu,j,k}^{\sigma,\tau} = C_{\mu,k,j}^{\tau,\sigma} = C_{\mu,j,k}^{-\sigma,-\tau}. \tag{149}$$

These relationships cause all the distinct coefficients to be included among those for which either $\tau \geqslant \sigma \geqslant 0$ or $\tau \geqslant -\sigma \geqslant 0$. We examine first the case $\tau \geqslant \sigma \geqslant 0$ and define a new index ρ by $\rho = \tau - \sigma$. We start from the explicit formulas

$$C_{\rho,\sigma,\tau}^{\sigma,\tau} = \left(\frac{2\rho+1}{2\tau+1}\right)\frac{\tau!(2\sigma)!}{\rho!\sigma!} \tag{150}$$

and

$$C_{\rho+1,\sigma,\tau+1}^{\sigma,\tau} = \left(\frac{2\rho+3}{2\tau+3}\right)\frac{\rho!(2\sigma)!}{\rho!\sigma!}. \tag{151}$$

We first advance μ and k (keeping $j = \sigma$) with

$$\left(\frac{\mu+\rho}{2\mu+1}\right)C_{\mu,j,k}^{\sigma,\tau} = \left(\frac{k+\tau}{2k+1}\right)C_{\mu-1,j,k-1}^{\sigma,\tau} + \left(\frac{k-\tau+1}{2k+1}\right)C_{\mu-1,j,k+1}^{\sigma,\tau} - \left(\frac{\mu-\rho-1}{2\mu-3}\right)C_{\mu-2,j,k}^{\sigma,\tau}. \tag{152}$$

In eq. (152) and the other recurrence relations to follow, note that $C_{\mu,j,k}^{\sigma,\tau} = 0$ if $j = |\sigma| - 1$, if $k = |\tau| - 1$, if $\mu = \rho - 1$, if $\mu + j + k$ is not even, or if $|j-k| \leqslant \mu \leqslant j + k$ is not satisfied.

These restrictions cause eq. (152) to suffice for the generation of all coefficients of the form $C^{\sigma,\tau}_{\mu,\sigma,k}$. Then the lower index j may be raised with the aid of

$$\left(\frac{j-\sigma}{2j-1}\right) C^{\sigma,\tau}_{\mu,j,k} = \left(\frac{k+\tau}{2k+1}\right) C^{\sigma,\tau}_{\mu,j-1,k-1} - \left(\frac{j+\sigma-1}{2j-1}\right) C^{\sigma,\tau}_{\mu,j-2,k} + \left(\frac{k-\tau+1}{2k+1}\right) C^{\sigma,\tau}_{\mu,j-1,k+1}. \quad (153)$$

We turn now to the case $\tau \geqslant -\sigma \geqslant 0$. To simplify the notation we set $-\sigma = \nu$, so that $\rho = \tau + \nu$. We start in this case from the explicit formulae

$$C^{-\nu,\tau}_{\rho,\nu,\tau} = \frac{\rho\,!(2\nu)\,!(2\tau)\,!}{(2\rho)\,!\nu\,!\tau\,!} \quad (154)$$

and

$$C^{-\nu,\tau}_{\rho+1,\nu,\tau+1} = \frac{\rho\,!(2\nu)\,!(2\tau+1)\,!}{(2\rho+1)\,!\nu\,!\tau\,!}. \quad (155)$$

The formula for advancing μ and k is now

$$\left(\frac{k-\tau}{2k-1}\right) C^{-\nu,\tau}_{\mu,j,k} = \left(\frac{\mu-\rho}{2\mu-1}\right) C^{-\nu,\tau}_{\mu-1,j,k-1} + \left(\frac{\mu+\rho+1}{2\mu+3}\right) C^{-\nu,\tau}_{\mu+1,j,k-1} - \left(\frac{k+\tau-1}{2k-1}\right) C^{-\nu,\tau}_{\mu,j,k-2} \quad (156)$$

and the formula for raising j is

$$\left(\frac{j-\nu}{2j-1}\right) C^{-\nu,\tau}_{\mu,j,k} = \left(\frac{\mu-\rho}{2\mu-1}\right) C^{-\nu,\tau}_{\mu-1,j-1,k} - \left(\frac{j+\nu-1}{2j-1}\right) C^{-\nu,\tau}_{\mu,j-2,k} + \left(\frac{\mu+\rho+1}{2\mu+3}\right) C^{-\nu,\tau}_{\mu+1,j-1,k}. \quad (157)$$

APPENDIX C

Bessel Functions and Related Integrals

In this work we use three types of spherical Bessel function, defined in terms of the corresponding ordinary Bessel functions by the formulae:

$$i_n(x) = (-1)^n \left(\frac{\pi}{2x}\right)^{1/2} I_{n+\frac{1}{2}}(x) \tag{158}$$

$$j_n(x) = \left(\frac{\pi}{2x}\right)^{1/2} J_{n+\frac{1}{2}}(x) \tag{159}$$

$$k_n(x) = \left(\frac{2}{\pi x}\right)^{1/2} K_{n+\frac{1}{2}}(x) \tag{160}$$

The ordinary Bessel functions I_n, J_n, and K_n are as defined by Watson (1952). These spherical Bessel functions satisfy the following recurrence relations:

$$\left(\frac{2n+1}{x}\right) i_n(x) = i_{n+1}(x) - i_{n-1}(x) \tag{161}$$

$$\left(\frac{2n+1}{x}\right) j_n(x) = j_{n+1}(x) + j_{n-1}(x) \tag{162}$$

$$\left(\frac{2n+1}{x}\right) k_n(x) = k_{n+1}(x) - k_{n-1}(x) \tag{163}$$

Starting points for the recurrence relations are the special values

$$i_0(x) = x^{-1} \sin x \tag{164}$$

$$i_{-1}(x) = -x^{-1} \cosh x \tag{165}$$

$$j_0(x) = x^{-1} \sin x \tag{166}$$

$$j_{-1}(x) = x^{-1} \cos x \tag{167}$$

$$k_0(x) = x^{-1} e^{-x} \tag{168}$$

$$k_{-1}(x) = x^{-1} e^{-x} \tag{169}$$

The functions $k_n(x)$ are calculated by direct use of the recurrence relation, eq. (163), starting from eqs. (168) and (169). Unfortunately, this approach is numerically unsatisfactory for the functions $i_n(x)$, and it has proved necessary to resort to more indirect methods for their evaluation. Following Corbató (1956), we have found it convenient to generate the $i_n(x)$ by use of eq. (161) to proceed from higher to lower n values. This is accomplished by

assuming $i_{N+1}(x) = 0$ for some sufficiently large N, and applying eq. (161) to the ratios of successive n values. As the index n decreases, the $i_n(x)$ generated in this way become successively more accurate. We proceed by defining

$$r_n(x) = i_{n+1}(x)/i_n(x), \tag{170}$$

and we rearrange eq. (161) to the form

$$r_{n-1}(x) = \frac{-x}{2n + 1 - xr_n(x)}. \tag{171}$$

Then, starting from $r_n = 0$, we may generate r_n by downward recurrence until we reach r_0. Then, starting from the computationally convenient formula for i_0,

$$i_0(x) = \frac{e^{|x|}}{1 + |x| - xr_0(x)}, \tag{172}$$

we successively determine the $i_n(x)$ for increasing n by use of the previously obtained r_n values and eq. (170).

We have not found it necessary to compute values of $j_n(x)$ in the present work, as these functions appear only in integrals which are evaluated analytically.

The integral $I^{\nu}_{\mu q}(\zeta)$ which appears in eq. (36) of the main text is essentially a generalization of the spherical Bessel function $i_\mu(\zeta)$. In particular,

$$I^0_{\mu 0}(\zeta) = 2i_\mu(\zeta). \tag{173}$$

Equation (173) may be proved by induction. Direct integration verifies eq. (173) for μ values of zero and unity. To proceed to higher μ values we show that $I^0_{\mu 0}$ satisfies the same recurrence relation as i_μ. To prove this, integrate eq. (36) by parts, thereby obtaining $(1 - \eta^2)^{1/2} P^1_\mu(\eta)$ in the integrand. Then use eq. (132) to eliminate P^1_μ.

Partial integrations of eq. (36) for $I^{\nu}_{\mu 0}$ lead to the further relation

$$I^{\nu}_{\mu 0}(\zeta) = \zeta^{-|\nu|} I^0_{\mu 0}(\zeta). \tag{174}$$

The remaining $I^{\nu}_{\mu q}$ are related to those already discussed by a recurrence relation connecting functions of contiguous q values. Introducing eq. (130) into eq. (36), we obtain

$$I^{\nu}_{\mu q}(\zeta) = \left(\frac{\mu + |\nu| + 1}{2\mu + 1}\right) I^{\nu}_{\mu+1,q-1}(\zeta) + \left(\frac{\mu - |\nu|}{2\mu + 1}\right) I^{\nu}_{\mu-1,q-1}(\zeta). \tag{175}$$

Equations (173)–(175) enable us to generate all the $I^{\nu}_{\mu q}(\zeta)$, starting from the $i_{\mu}(\zeta)$.

In eqs. (20) and (21) two additional functions, $A_n(x)$ and $B_n(x)$, enter the evaluation of the one-electron integrals. These functions are closely related to the Bessel functions $k_n(x)$ and $i_n(x)$. The simplest way of evaluating $A_n(x)$ is through its recurrence formula, obtained by partial integration:

$$A_n(x) = \frac{n}{x} A_{n-1}(x) + A_0(x). \tag{176}$$

To start the recurrence process we need

$$A_0(x) = x^{-1} e^{-x}. \tag{177}$$

The recurrence formula for $B_n(x)$ is computationally unsatisfactory, and the $B_n(x)$ are best computed by means dependent upon their relationship to the $i_n(x)$. Comparing with eq. (36), we see that

$$B_n(x) = I^0_{0n}(x). \tag{178}$$

Direct use of eq. (178) is cumbersome if the I^0_{0n} are not needed for other purposes, but the repeated use of eq. (175) to produce I^0_{0n} can be shown to be equivalent to the explicit formula

$$B_n(x) = 2 \sum_{\mu=0,1}^{n}{}' \frac{n!(2\mu + 1)}{(n - \mu)!!(n + \mu + 1)!!} i_{\mu}(x). \tag{179}$$

Here the prime indicates that the summation is over alternate μ values of the same parity as n, and $n!!$ stands for

$$n(n - 2)(n - 4) \ldots (2 \text{ or } 1).$$

The $A_n(x)$ are related to the $k_n(x)$ in a way parallel to eq. (179):

$$A_n(x) = \sum_{\mu=0,1}^{n}{}' \frac{n!(2\mu + 1)}{(n - \mu)!!(n + \mu + 1)!!} k_{\mu}(x). \tag{180}$$

However, we do not actually use eq. (180) for computation, since eq. (176) proves to be more convenient.

APPENDIX D

Integrals of Legendre Functions

The formulae of this Section become much more compact if we use the modified definitions $\mathscr{P}_l^m$ and $\mathscr{Q}_l^m$ for the Legendre functions. Then the integrals under discussion become

$$K_{\mu p}^{\nu} = \int_1^{\Xi} e^{-\delta\xi}\, \xi^p \mathscr{P}_{\mu}^{\nu}(\xi)\, d\xi \tag{181}$$

and

$$L_{\mu p}^{\nu} = \int_{\Xi}^{\infty} e^{-\delta\xi}\, \xi^p \mathscr{Q}_{\mu}^{\nu}(\xi)\, d\xi. \tag{182}$$

The method for evaluation of $K_{\mu p}^{\nu}$ depends upon the value of $\delta(\Xi - 1)$. Repeated partial integrations of eq. (181) for $K_{\mu 0}^{\nu}$ leads to

$$K_{\mu,0}^{\nu}(\Xi, \delta) = e^{-\delta\Xi} \sum_{j=0}^{\infty} \delta^j \mathscr{P}_{\mu}^{|\nu|+j+1}(\Xi). \tag{183}$$

Equation (183) is satisfactory for small $\delta(\Xi - 1)$. For values of $\delta(\Xi - 1)$ too large to permit rapid convergence of eq. (183), it is more useful to integrate eq. (181) by parts once, bringing the result after some manipulation into the form

$$\left(\frac{2\mu + 1}{\delta}\right) [K_{\mu,0}^{\nu}(\Xi, \delta) - e^{-\delta\Xi} \mathscr{P}_{\mu}^{\nu+1}(\Xi)] = K_{\mu+1,0}^{\nu}(\Xi, \delta) - K_{\mu-1,0}^{\nu}(\Xi, \delta). \tag{184}$$

A comparison of eq. (183) for different ν values leads to another useful formula:

$$\delta^{|\nu|} K_{\mu,0}^{\nu}(\Xi, \delta) = K_{\mu,0}^{0}(\Xi, \delta) - e^{-\delta\Xi} \sum_{j=0}^{|\nu|-1} \delta^j \mathscr{P}_{\mu}^{j+1}(\Xi). \tag{185}$$

Equations (184) and (185) permit initial values of K_{00}^0 and K_{10}^0 to be extended to arbitrary values of μ and ν. These formulae work well at large $\delta(\Xi - 1)$. The minimum value of $\delta(\Xi - 1)$ at which eqs. (184) and (185) are sufficiently accurate determines the upper end of the range of use of eq. (183).

The starting values needed to use eqs. (184) and (185) are obtained by direct integration:

$$K_{0,0}^{0}(\Xi, \delta) = \delta^{-1}(e^{-\delta} - e^{-\delta\Xi}) \tag{186}$$

and

$$K^0_{1,0}(\Xi, \delta) = \delta^{-1}[(1 + \delta^{-1})\, e^{-\delta} - (\Xi + \delta^{-1})\, e^{-\delta\Xi}]. \quad (187)$$

After obtaining, by one of the above methods, a sufficient set of $K^\nu_{\mu 0}$, the index p of $K^\nu_{\mu p}$ is raised with the aid of the recurrence formula

$$K^\nu_{\mu p}(\Xi, \delta) = \left(\frac{\mu + |\nu| + 1}{2\mu + 1}\right) K^\nu_{\mu+1,p-1}(\Xi, \delta) + \left(\frac{\mu - |\nu|}{2\mu + 1}\right) K^\nu_{\mu-1,p-1}(\Xi, \delta). \quad (188)$$

Further details of this analysis may be found in earlier work (Harris, 1960).

For the two-center integrals we encounter the $K^\nu_{\mu p}$ for the special case $\Xi \to \infty$. In this case, the $K^\nu_{\mu p}(\Xi, \delta)$ reduce to simpler forms which are analogous to the $I^\nu_{\mu q}(\zeta)$ discussed in Appendix C. In particular,

$$K^0_{\mu 0}(\infty, \delta) = k_\mu(\delta) \quad (189)$$

and

$$K^0_{0p}(\infty, \delta) = A_p(\delta). \quad (190)$$

We find that, at $\Xi \to \infty$, only the $K^0_{0p}(\infty, \delta)$ contribute to the two-center integrals. The simple recurrence formula for $A_p(\delta)$ then makes it particularly advantageous to use eq. (190).

It is possible to evaluate the $L^\nu_{\mu p}(\Xi, \delta)$ by analytical methods such as those described for the $K^\nu_{\mu p}$. However, for some ranges of the variables Ξ and δ we were unable to find analytical methods which were computationally entirely satisfactory, as the equations corresponding to eq. (184) could not be used with good results either for ascending or descending μ. Our solution was to integrate certain of the $L^\nu_{\mu p}$ numerically, following which analytical procedures sufficed to obtain the remaining $L^\nu_{\mu p}$.

We applied the numerical integration to the $L^1_{\mu 0}$, whether or not values for $\nu = 1$ were needed in the calculations. We chose $L^1_{\mu 0}$ rather than $L^0_{\mu 0}$ because the integrand of the former is bounded for all Ξ values, while, in $L^0_{\mu 0}$, the factor $\mathcal{Q}^0_\mu(\xi)$ increases without limit as ξ approaches unity. After obtaining the $L^1_{\mu 0}$ by methods

described in detail below, we generated $L^{\nu}_{\mu 0}$ for other ν values (both $\nu = 0$ and $\nu > 1$) by use of

$$L^{\nu}_{\mu 0}(\Xi, \delta) + e^{-\delta\Xi} \mathcal{Q}^{|\nu|+1}_{\mu}(\Xi) = \delta L^{|\nu|+1}_{\mu 0}(\Xi, \delta). \tag{191}$$

Advancement of the index p is by the analogue of eq. (188):

$$L^{\nu}_{\mu,p}(\Xi, \delta) = \left(\frac{\mu + |\nu| + 1)}{2\mu + 1}\right) L^{\nu}_{\mu+1,p-1}(\Xi, \delta) + \left(\frac{\mu - |\nu|}{2\mu + 1}\right) L^{\nu}_{\mu-1,p-1}(\Xi, \delta). \tag{192}$$

As discussed above, the starting set of integrals $L^{1}_{\mu 0}$ were evaluated numerically. From eq. (182) we have

$$L^{1}_{\mu 0}(\Xi, \delta) = \int_{\Xi}^{\infty} e^{-\delta\xi} \mathcal{Q}^{1}_{\mu}(\xi)\, d\xi. \tag{193}$$

Equation (193) is of the generalized form for Gauss–Laguerre quadrature (Rabinowitz and Weiss, 1959) provided that proper account is taken of the scaling factor δ. We have

$$L^{1}_{\mu 0}(\Xi, \delta) = e^{-\delta\Xi} \sum_{k=1}^{N} w_k \mathcal{Q}^{1}_{\mu}(\delta^{-1} y_k + \Xi), \tag{194}$$

where w_k and y_k are the quadrative weights and points, respectively. Equation (194) provides at least six significant figures for all $L^{1}_{\mu 0}$, $\mu < 25$, with $N \geqslant 32$. However, we found that eq. (193) could be evaluated to still higher accuracy by first converting the integration interval to $(-1, 1)$ and then applying 32-point Lobatto quadrature (Michels, 1963). The Legendre functions $\mathcal{Q}^{1}_{\mu}$ were evaluated in either case by the methods described in Appendix B.

A slight complication arises from this numerical approach in that L^{0}_{00} cannot be obtained by the method described above because the $\mathcal{Q}^{m}_{l}$ are not defined for $l < |m|$. We therefore evaluate L^{0}_{00} directly from the explicit formula

$$L^{0}_{00}(\Xi, \delta) = \frac{e^{-\delta\Xi}}{\delta}\left(Q_0(\Xi) - \tfrac{1}{2}[F_1(\delta\Xi - \delta) - F_1(\delta\Xi + \delta)]\right). \tag{195}$$

Here $F_1(x)$ is an exponential integral defined as

$$F_1(x) = e^{x} \int_{x}^{\infty} t^{-1} e^{-t}\, dt.$$

We evaluate $F_1(x)$ by rational polynomial approximations (Hastings, 1955).

Finally, we consider the $L_{\mu\nu}(\Xi, \delta)$ in the special case $\Xi = 1$. The methods outlined above present no difficulties in this case, except that it is now helpful to use eq. (148) for $\mathscr{Q}_l^m(1)$, and to use the limiting form of eq. (195):

$$L_{00}^{\upsilon}(1, \delta) = \frac{e^{-\delta}}{2\delta}[\ln(2\delta) + \gamma + F_1(2\delta)]. \tag{196}$$

Here γ is Euler's constant, 0·5772156649 . . . .

APPENDIX E

Fourier Transforms of Slater-type Orbitals

The quantity $(n, l, \delta)^T$ given in integral form in eq. (60) is proportional to the radial dependence of the Fourier transform of $r^n e^{-\delta r} P_l(\cos\theta)$ and has an explicit representation (Geller, 1963)

$$(n, l, \delta)^T = \frac{2^l l!(n - l + 1)!\delta^{n-l+1}k^l}{(k^2 + \delta^2)^{n+2}} \times \sum_{s=0}^{\leqslant \frac{1}{2}(n-l+1)} (-1)^s \binom{n + l + 2}{2s + 2l + 1}\binom{s + l}{s}\left(\frac{k}{\delta}\right)^{2s}. \tag{197}$$

From eq. (197), or more conveniently from eq. (60) and the properties of spherical Bessel functions, a number of recurrence relations involving the $(n, l, \delta)^T$ may be deduced. Some of these are

$$k(n, l, \delta)^T + (n - l)(n - 1, l + 1, \delta)^T = \delta(n, l + 1, \delta)^T \tag{198}$$

$$(n, l + 1, \delta)^T + (n, l - 1, \delta)^T = \left(\frac{2l + 1}{k}\right)(n - 1, l, \delta)^T \tag{199}$$

$$(n + l + 2)(n, l - 1, \delta)^T + (n - l + 1)(n, l + 1, \delta)^T = \delta\left(\frac{2l + 1}{k}\right)(n, l, \delta)^T \tag{200}$$

$$\delta(n, l, \delta)^T + k(n, l + 1, \delta)^T = (n + l + 2)(n - 1, l, \delta)^T \tag{201}$$

$$(k^2 + \delta^2)(n, l, \delta)^T + (n - l)k(n - 1, l + 1, \delta)^T = (n + l + 2)\delta(n - 1, l, \delta)^T \quad (202)$$

$$(k^2 + \delta^2)(n, l, \delta)^T + (n + l)(n - l - 1)(n - 2, l, \delta)^T = 2n\delta(n - 1, l, \delta)^T \quad (203)$$

$$(n + l + 2)k(n - 1, l, \delta)^T + (n - l)\delta(n - 1, l + 1, \delta)^T = (k^2 + \delta^2)(n, l + 1, \delta)^T \quad (204)$$

$$(l - 1, l, \delta)^T = \left(\frac{2lk}{k^2 + \delta^2}\right)(l - 2, l - 1, \delta)^T \quad (205)$$

$$(l, l, \delta)^T = \frac{(2l + 2)\delta}{k^2 + \delta^2}(l - 1, l, \delta)^T \quad (206)$$

Equations (198)–(206) permit the stepwise generation of all $(n, l, \delta)^T$ for $n + 1 \geqslant l \geqslant 0$ in steps, starting from $(-1, 0, \delta)^T$, which has the well-known value

$$(-1, 0, \delta)^T = (k^2 + \delta^2)^{-1}. \quad (207)$$

APPENDIX F

Expansion Formulae for Slater-type Orbitals

Equation (106) of the main text gives the basic formula for the expansion of a Slater-type orbital about a displaced origin. After eq. (106) appears a summary of the coordinate notation applying both to that equation and to the discussion of this Appendix. Before discussing the evaluation of the coefficients $V^m_{n,l,j}(\delta r, \delta R)$, we note that in the special case $l = m = 0$, eq. (106) reduces to the Barnett–Coulson expansion (Barnett and Coulson, 1951; Barnett, 1963). Writing the Barnett–Coulson expansion in the form

$$r_a^{n-1} e^{-\delta r_a} = \delta^{-n} \sum_{j=0}^{\infty} (-1)^j \frac{(2j + 1)}{\sqrt{Rr}} \zeta_{nj}(\delta r, \delta R) P_j(\cos\theta), \quad (208)$$

we see that the present coefficients and the Barnett–Coulson coefficients are related by

$$V^0_{n0j}(\delta r, \delta R) = \frac{(-1)^j(2j + 1)}{\delta\sqrt{Rr}} \zeta_{nj}(\delta r, \delta R). \quad (209)$$

The first step in evaluating the $V^m_{n,l,j}$ is to obtain the formal solution

$$V^m_{n,l,j}(\delta r, \delta R) = \delta^{n-1}\left(\frac{2j+1}{2}\right)\frac{(j-|m|)!}{(j+|m|)!} \times \int_0^\pi r_a^{n-1}\, e^{-\delta r_a} P^m_l(\cos\theta_a) P^m_j(\cos\theta)\sin\theta\, d\theta. \quad (210)$$

In certain cases eq. (210) may be integrated:

$$V^0_{n,0,0}(\delta r, \delta R) = \frac{\delta^{n-1}|R-r|^{n+1}}{2rR} A_n(\delta|R-r|) - \frac{\delta^{n-1}(R+r)^{n+1}}{2rR} A_n\Big(\delta(R+r)\Big) \quad (211)$$

$$V^0_{0,0,j}(\delta r, \delta R) = (2j+1)k_j(\delta r_+)i_j(\delta r_-), \quad (212)$$

where r_+ and r_- are the greater and lesser of R and r, and i_j, k_j, and A_n are all functions defined in Appendix C. Equations (211) and (212) have been given by Barnett (1963).

The $V^m_{n,l,j}$ coefficients with more general index values can be obtained recursively, starting from those given in eqs. (211) and (212). The necessary recurrence relations have been reported by the authors (Harris and Michels, 1965b), and are listed below. These recurrence formulae apply for $n \geqslant l \geqslant m \geqslant 0$, $j \geqslant m$, with the convention that $V^\alpha_{\beta,\gamma,\delta} = 0$ whenever $\gamma < \alpha$, $\delta < \alpha$, or $\beta < \gamma$.

$$V^m_{n+2,l,j} = \delta^2(R^2+r^2)V^m_{n,l,j} + 2\delta^2 rR\left[\left(\frac{j-m}{2j-1}\right)V^m_{n,l,j-1} + \left(\frac{j+m+1}{2j+3}\right)V^m_{n,l,j+1}\right] \quad (213)$$

$$\left(\frac{l-m+1}{2l+1}\right)V^m_{n+1,l+1,j} + \left(\frac{l+m}{2l+1}\right)V^m_{n+1,l-1,j} = \delta R V^m_{n,l,j} + \delta r\left[\left(\frac{j-m}{2j-1}\right)V^m_{n,l,j-1} + \left(\frac{j+m+1}{2j+3}\right)V^m_{n,l,j+1}\right] \quad (214)$$

$$2\delta R\left[\left(\frac{l-m+1}{2l+1}\right)V^m_{n+1,l+1,j} + \left(\frac{l+m}{2l+1}\right)V^m_{n+1,l-1,j}\right] = \delta^2(R^2-r^2)V^m_{n,l,j} + V^m_{n+2,l,j} \quad (215)$$

$$V^{m+1}_{n+1,l-1,j+1} - V^{m+1}_{n+1,l+1,j+1} = (2l+1)\delta r\left[\left(\frac{1}{2j+5}\right)V^{m}_{n,l,j+2} - \left(\frac{1}{2j+1}\right)V^{m}_{n,l,j}\right] \quad (216)$$

$$(l-m+2)(l-m+1)V^{m-1}_{n+1,l+1,j-1} - (l+m)(l+m-1)V^{m-1}_{n+1,l-1,j-1} = (2l+1)\delta r\left[\frac{(j-m)(j-m-1)}{2j-3}V^{m}_{n,l,j-2} - \frac{(j+m)(j+m-1)}{2j+1}V^{m}_{n,l,j}\right] \quad (217)$$

$$\left(\frac{2m-1}{\delta R}\right)V^{m-1}_{n,m-1,j} = (n-m)\,V^{m}_{n-1,m,j} - V^{m}_{n,m,j} \quad (218)$$

$$\left(\frac{2m-1}{\delta R}\right)[V^{m-1}_{n,m-1,j} + V^{m-1}_{n+1,m-1,j}] = (n-m)[V^{m}_{n,m,j} + V^{m}_{n-1,m,j}] - V^{m}_{n+1,m,j} \quad (219)$$

$$\frac{1}{\delta^2 Rr}V^{m}_{n+1,m,j} = -(n-m)\left[\left(\frac{1}{2j+3}\right)V^{m}_{n-1,m,j+1} - \left(\frac{1}{2j-1}\right)V^{m}_{n-1,m,j-1}\right] + \left[\left(\frac{1}{2j+3}\right)V^{m}_{n,m,j+1} - \left(\frac{1}{2j-1}\right)V^{m}_{n,m,j-1}\right] \quad (220)$$

$$V^{m}_{m+1,m,j} = -\left(\frac{2m-1}{\delta R}\right)(V^{m-1}_{m,m-1,j} + V^{m-1}_{m+1,m-1,j}) \quad (221)$$

$$V^{0}_{n+1,0,0} = (n+1)\,V^{0}_{n,0,0} + \frac{(\delta|R-r|)^{n+1}}{2\delta^2 Rr}\,e^{-\delta|R-r|} - \frac{(\delta(R+r))^{n+1}}{2\delta^2 Rr}\,e^{-\delta(R+r)} \quad (222)$$

For the special case $l = m = 0$, eqs. (213), (220), and (222) reduce to expression previously reported by Barnett (1963).

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Note added in proof (see p. 246): Recent program modifications which involve a more efficient handling of the many Clebsch–Gordan coefficients have reduced the average computation time to 30—50 msec per integral with Univac 1108 equipment.

THE LOCAL POTENTIAL APPLIED TO INSTABILITY PROBLEMS

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I. INTRODUCTION

In chemistry, physics, and engineering, as well as other fields, the representation of physical processes by macroscopic mathematical models involving complex partial differential equations is a well-recognized route of analysis. Detailed analytical solutions of these equations for given initial and boundary conditions usually prove prohibitive, but certain specific questions of interest can be answered by analytical treatment. We are concerned with the stability of a system, in which mass, momentum, and heat are transferred, and in particular wish to predict whether or not an initially stable system will become unstable.

In the classical treatment of stability the phenomenological equations of change are linearized about some steady or unperturbed state. One presumes that an arbitrary disturbance develops in one of the parameters in the model, a disturbance which can be expressed as a sum of normal modes comprising a complete set over the state space. Since the model is linear and the presumed disturbances are small, the response of the model can be

determined by superimposing the responses to each of the individual normal modes. Predicting stability is then reduced to examinating model solutions with a time-dependence proportional to $e^{-\sigma t}$, where σ is termed the stability parameter. One states that those non-trivial solutions of the model for which the real part of σ is less than 0 are unstable because any small perturbation will grow without bound and instability develops in a related physical system. To sum up, one seeks to answer the question: does an initial disturbance grow with time? More detailed consideration of the criteria for stability can be found in the references in Stuart[21] and in Case[2] and Chandrasekhar.[3]

A model of a physical process formulated in terms of differential equations can be transformed through the use of the calculus of variations into an integral representation. A familiar example is the Newtonian equations of motion which in their alternate variational formulation, based on the concept of energy, are called Hamilton's principle. In applying stability analysis to a particular problem one is often faced with the necessity of integrating a system of linear differential equations and of simultaneously determining the growth parameter σ. It is precisely this step of the analysis which often proves to be so complicated that an exact result is unattainable. In these cases it is convenient to have a variational statement of the characteristic value problem as an aid in establishing an approximate solution. Chandrasekhar[3] makes use of this approach. However, to date the formulation of a variational principle which has the characteristic value problems as its Euler–Lagrange equations has been mainly heuristic in nature rather than based on clearly defined physical principles.[6,10,13,17,18,19]

More recently, Glansdorff and Prigogine[7,8,12] have formulated a variational principle based on fluctuation theory which has the characteristic value problem as its Euler–Lagrange equations. They introduced the concept of the local potential and demonstrated the applicability of this concept to continuum systems. Schechter and Himmelblau[14] have applied these principles to the Bénard problem and have demonstrated that the concepts of Glansdorff and Prigogine can yield an appropriate variational statement which can be employed to treat stability problems. While the variational approach described here is only one of

many possible methods of using the calculus of variations to assist in the study of stability, it appears to have considerable merit in comparison with other variational formulations of transport phenomena problems.

We first present below a general theoretical stability analysis based on the variational principle of Glansdorff and Prigogine, then make predictions of marginal stability for a special case, namely, the physical process of gas absorption, and finally compare the predictions with experimental results.

II. GENERAL STABILITY ANALYSIS

Glansdorff and Prigogine have shown that there exists a quantity of the form

$$\delta\phi = \int_V (Q_i \delta X_i)\, dV \leqq 0 \tag{1}$$

where ϕ is termed the local potential, Q_i and X_i are the generalized fluxes and forces of irreversible thermodynamics, respectively, and V is the system volume. Local potentials are quadratic functions and can be related to the probability of the fluctuation of a thermodynamic variable from its expected value, both in the stationary and in time-dependent states. Such fluctuations occur on a time scale of considerably less magnitude than is relevant for the shifts which occur in the expected value induced by a disturbance at one of the system boundaries. $\delta\phi$ can be shown to be a type of generalized entropy production and has the following significance: for a system with time-independent boundary conditions and dissipative components, $\delta\phi$ is always an increasing function of time and reaches an extremum. A detailed explanation of the local potential can be found in works by Glansdorff and Prigogine.[7,15]

In what follows we shall distinguish between a fluctuating variable and its expected value by assigning an asterisk(*) to the expected values of parameters and dependent variables. Consequently,

$$\begin{aligned} \delta\rho_\alpha(x_i, t) &= \rho_\alpha(x_i, t) - \rho_\alpha^*(x_i, t) \\ \delta v_i(x_i, t) &= v_i(x_i, t) - v_i^*(x_i, t) \\ \delta T(x_i, t) &= T(x_i, t) - T^*(x_i, t) \end{aligned} \tag{2}$$

where $x_i\,(i = 1, 2, 3)$ are the position coordinates, $v_i\,(i = 1, 2, 3)$ are the velocity components, ρ_α is the mass of component α per unit volume, and T is the absolute temperature. The treatment of transport processes by the concept of the local potential has the very useful feature that time-dependent processes can be encompassed by the analysis if one extends the definition of the local potential so that both the fluctuating and the expected functions are taken to be time-dependent as indicated by eq. (2).

Schechter and Himmelblau have postulated that for a very general class of transport problems described by macroscopic models of continuum theory the starting point in formulating an appropriate stability criterion is to compose the local potential in the following form:

$$\delta\phi(J, J^*) = \int_V F(J, J^*)\,\mathrm{d}V \leqq 0, \tag{3}$$

where J's represent separate sets of variables, as for example

$$J = \{v_i, t), \rho_\alpha(x_i, t)\}$$

and

$$J^* = \{v_i^*(x_i, t), \rho_i^*(x_i, t)\}.$$

The quantity ϕ is defined by withdrawing the operator δ from within the integral in eq. (1) by assigning the velocities, pressure, density, temperature, their derivatives, and other terms that are coefficients of the fluctuations appearing in eq. (1) to be known functions at their expected values and hence not subject to variation. An example to clarify the technique and the abstract notation is presented in the next Section.

We can then in general write a functional of the following structure:

$$\begin{aligned} L = \int_0^\theta \phi\,\mathrm{d}t = &\int_0^\theta \int_V (J_{(1)}, J_{(2)} \cdots, J_{(N)}; J^*_{(1)}, I^*_{(2)} \cdots, J^*_{(N)})\,\mathrm{d}V\,\mathrm{d}t \\ &+ \int_0^\theta \int_S (J_{(1)}, J_{(2)} \cdots, J_{(N)};\ J^*_{(1)}, J^*_{(2)} \cdots, J^*_{(N)})\,\mathrm{d}S\,\mathrm{d}t \\ &+ \int_0^\theta \int_V \sum_{q=1}^{N} a^*_{(q)} \frac{\partial J^*_{(q)}}{\partial t} J_{(q)}\,\mathrm{d}V\,\mathrm{d}t, \end{aligned} \tag{4}$$

such that the functions $J_{(1)} \cdots J_{(N)}$ which make L an extremal and at that state satisfy

$$J_{(q)} = J^*_{(q)} \tag{5}$$

are the properties defining the evolution of the system. The $J^*_{(q)}$ and the $a^*_{(q)}$ are *presumed* to be known functions of position and time and are not subject to variation. The second (the surface) integral on the right-hand side of eq. (4) evolves during application of the divergence theorem to eq. (1), demonstrating that the boundary conditions are included in the variational formulation, while the third integral contains the time derivatives. The symbol θ represents some very short time because we are interested solely in the initial growth, or decay, of disturbances from the steady state at which $t = 0$.

In order to visualize how the stability parameter σ is introduced into eq. (4), we assume that both the starred and unstarred J's can be split into time-dependent quantities and a time-dependent quantity as follows

$$\begin{aligned} J_{(q)} &= J^s_{(q)}(x_i) + j_{(q)}(x_i)\, \mathrm{e}^{-\sigma t} \qquad q = 1, \ldots, N \\ J^*_{(q)} &= J^s_{(q)}(x_i) + j^*_{(q)}(x_i)\, \mathrm{e}^{-\sigma^* t} \qquad q = 1, \ldots, N \end{aligned} \tag{7}$$

in which $J^s_{(q)}$ is $J_{(q)}$ at the stationary state, and $j_{(q)}$ is the perturbation from this stationary state.

In principle, eqs. (6) and (7) could be introduced into (4), the integrations carried out, and then an extremal found for L, but as a practical matter Schechter and Himmelblau suggested instead that, after integration over time, for small θ, L can be expanded as follows:

$$L \cong \theta p_1 + \frac{\theta^2}{2} p_2 = \tilde{L} \tag{8}$$

where

$$p_1 = E|_{t=0} - \sigma^* \int_V \left\{ \sum_{q=1}^{N} a^*_{(q)} j^*_{(q)} (J^s_{(p)} + j_{(p)}) \right\} \mathrm{d}V; \tag{9}$$

$$p_2 = \left(\frac{\partial E}{\partial t} \right)_{t=0} - \sigma^* \frac{\partial}{\partial t} \times \left\{ \int_V \left[\sum_{q=1}^{N} a^*_{(q)} (J^s_{(q)} + j_{(q)} \mathrm{e}^{-\sigma t}) j^*_{(q)} \mathrm{e}^{-\sigma^* t} \right] \mathrm{d}V \right\}_{t=0} \tag{10}$$

$$E = \int_V [\sum_{q=1}^{N} (J^s_{(q)} + j^*_{(q)} e^{-\sigma^* t})][J^s_{(p)} + j_{(p)} e^{-\sigma t}] \, dV$$
$$+ \int_S [\sum_{q=1}^{N} (J^s_{(q)} + j^*_{(q)} e^{-\sigma t})][J^s_{(p)} + j_{(p)} e^{-\sigma t}] \, dS. \quad (11)$$

While it is true that $\tilde{L}$ does not represent exactly the same variational formulation as eq. (4), and that, if eq. (6) provides an extremal for $\tilde{L}$, eq. (6) will not simultaneously provide an exact extremal for (4), one can heuristically view the truncation in (8) as having an asymptotically diminishing effect as $\theta \to 0$, or alternately can take into account higher-order terms in θ.

If the $j_{(q)}(x_i)$ and σ are to be chosen so that $\tilde{L}$ is rendered stationary, we take the variation in $\tilde{L}$

$$\delta \tilde{L} = \theta \sum_{q=1}^{N} \frac{\delta p_1}{\delta j_{(q)}} \delta j_{(q)} + \frac{\theta^2}{2} \sum_{q=1}^{N} \frac{\delta p_2}{\delta j_{(q)}} \delta j_{(q)} + \frac{\theta^2}{2} \frac{\partial p_2}{\partial \sigma} d\sigma. \quad (12)$$

The quantity $\partial p_1 / \partial \sigma$ vanishes and, consequently, is omitted from eq. (12). For $\tilde{L}$ to be stationary, it is necessary that

$$\frac{\delta p_1}{\delta j_{(q)}} = 0 \qquad q = 1, \ldots, N \quad (13)$$

and

$$\frac{\partial p_2}{\partial \sigma} = 0 \qquad q = 1, \ldots, N. \quad (14)$$

This system of equations makes it possible to determine the N functions $j_{(q)}$ and the decay rate parameter, σ. The latter is obtained directly from eq. (14), after application of eq. (5)

$$\sigma = \frac{-\left[\frac{\partial E}{\partial (\sigma t)}\right]_{t=0}}{\int_V [\sum_{q=1}^{N} a_{(q)} j_{(q)} j_{(q)}] \, dV}; \quad (15)$$

or it may come indirectly through eq. (13), as will be demonstrated in the next Section. The denominator of eq. (15) is always positive since $a_{(q)} > 0$. In certain special cases, the numerator can be shown to take on a fixed sign for all admissible $j_{(q)}$, and in these cases the sign of σ can be established without further calculation. However, for most problems the sign of σ cannot be determined

without specific knowledge of the perturbations, $j_{(q)}(x_i)$. To evaluate σ exactly, the differential equations generated by taking the variations indicated by eq. (13) must be solved simultaneously, a problem as difficult as the solution of the fundamental phenomenological equations comprising the basic model. However, the study of stability can be carried out adequately through the use of approximate solutions for the $j_{(q)}$. Assume

$$j_{(q)} = \sum_{k=1}^{r} b_{(k)}^{(q)} \psi_{(k)}(x_i), \tag{16}$$

where the $b_{(k)}^{(q)}$ are constants to be determined and the $\psi_{(k)}$ are predetermined functions of position.

For selection of the spacial dependence of $\psi_k(x_i)$, two principles must act as guides. These functions should be members of a family of functions comprising a complete set, and they should simultaneously satisfy the (*a*) boundary conditions, (*b*) mass balances, (*c*) momentum balance, and (*d*) energy balance, if an exact solution to the variational problem of determining the extremal defined by eq. (12) is to be obtained. However, functional formulations can be written which satisfy (*a*), (*b*), and (*d*), and which satisfy (*c*) only approximately, if only a few members of the complete set are used. While these functions will not provide exact solutions to the problem of interest, they *will* in many cases be adequate to evaluate stability.

Equation (9) then becomes:

$$\mathcal{P}_1 = E[b_{(k)}^{(q)}]_{t=0} - \sigma^* \int_V \{ \sum_{q=1}^{N} a^*{}_{(q)} (J_{(q)}^s + \sum_{k=1}^{r} b_{(k)}^{(q)} \psi_{(k)}) (\sum_{l=1}^{r} b_{(l)}^{*(q)} \psi_{(l)}) \} \, dV, \tag{17}$$

where

$$j_q^* = \sum_{l=1}^{r} b_{(l)}^{*(q)} \psi_{(l)}. \tag{18}$$

The coefficients $b_{(k)}^{(l)}$ are to be selected so that

$$\frac{\partial \mathcal{P}_1}{\partial b_{(k)}^{(q)}} = 0 \qquad \begin{matrix} q = 1, \ldots, N \\ k = 1, \ldots, r \end{matrix} \tag{19}$$

These $N \times r$ equations can be written as

$$0 = \frac{\partial E}{\partial b_k^q} - \sigma^* \int_V \{a_{(q)} \psi_k \sum_{l=1}^{r} b_l^{(q)} \psi_l\} \, dV \tag{20}$$

which is an eigenvalue problem since there are $N \times r$ homogeneous equations and the σ^* must be chosen so that a nontrivial solution exists. These values of σ^* then determine the system stability.

III. APPLICATION OF STABILITY ANALYSIS

To illustrate the concepts developed in the previous Section and provide an example to make the somewhat abstract notation more meaningful, we investigate in this Section the stability of a process involving laminar flow and simultaneous interphase mass transfer, a process not yet treated in the literature.

The concept of enhancing mass interphase transfer through the growth of instabilities is well known, especially for the cases of interfacial turbulence,[20] and diffusing liquid–liquid systems.[9,16,23] However, very little theoretical or experimental work has been reported on instabilities in gas–liquid interphase mass transfer across horizontal interfaces, a situation quite conducive to the generation of adverse density gradients. Tang and Himmelblau[22] investigated the absorption of carbon dioxide into water in a co-current flow horizontal duct for modest contact times, and found that a model of the transfer process which ignored the instability factor successfully predicted the experimental data. Similar observations were made by Danckwerts and Kennedy[5] for short times on a rotating drum apparatus. On the other hand, Danckwerts[4] has stated that the penetration theory for interphase transfer will hold for only short contact times for transfer between carbon dioxide and water because for longer contact times convection currents will arise since the density of a solution of carbon dioxide is greater than that of water and the system will become unstable. Furthermore, the Bénard problem,[3] which is somewhat comparable to the problem of interest, has for many years stood as a classical example of the prediction of the onset of instability.

A. Mathematical Model of the Process

Consider a horizontal layer of fluid in which mass transfer occurs in a downward vertical direction across a flat interface. Because of the mass transfer, an adverse density gradient will arise; that is, the fluid at the interface will be heavier than the fluid underneath the interface. Under these conditions the fluid is potentially unstable, and convection patterns can develop. For isothermal conditions the component mass and the momentum equations may be written as

$$\frac{\partial \rho_\alpha}{\partial t} = -\frac{\partial}{\partial x_j}(\rho_\alpha v_j) - \frac{\partial}{\partial x_j} J_j^{(\alpha)} + \sum_{\beta=1}^{R} M_{\alpha_\beta} v_\alpha K_\beta \tag{21}$$

where $J_j^{(\alpha)} = \rho_\alpha(v_{\alpha_i} - v_i)$,

M_α = molecular mass of component α,

$v_{\alpha\beta}$ = stoichiometric coefficient in β'th chemical reaction,

K_β = rate of reaction,

ρ = mass of phase per unit volume, and

ρ_α = concentration expressed as mass of component α per unit volume;

and

$$\rho \frac{\partial v_i}{\partial t} = -\rho v_j \frac{\partial v_i}{\partial x_j} - \frac{\partial \pi_{ij}}{\partial x_j} + \sum_{\alpha=1}^{N} \rho_\alpha F_i^{(\alpha)}, \tag{22}$$

where π_{ij} = stress tensor, and

$F_i^{(\alpha)}$ = external force acting on α.

It will be assumed that the boundary conditions are time-independent.

For the case where there is a low concentration of the solute in the solvent, several approximations can be made. It will be assumed that the solvent is incompressible, so that its density is constant. The overall density of the mixture will also be taken as constant. For no chemical reaction, the mass balances reduce to

$$\partial v_j / \partial x_j = 0 \tag{23}$$

for the solvent (α denotes the solvent); and

$$\frac{\partial \rho_\beta}{\partial t} = -\frac{\partial}{\partial x_j}(\rho_\beta v_j + J_j^{(\beta)}) \tag{24}$$

for the solute (β denotes the solute). For an incompressible fluid the momentum balance becomes

$$\rho_0 \frac{\partial v_i}{\partial t} = -\rho_0 v_j \frac{\partial v_i}{\partial x_j} - \frac{\partial p}{\partial x_i} + \mu \frac{\partial^2 v_i}{\partial x_j^2} + \rho_{\alpha_0} F_i^{(\alpha)} + \rho_\beta F_i^{(\beta)}, \tag{25}$$

where the subscript 0 refers to constant values of solution and solvent density. Note that these are analogous to the Boussinesq approximations.

For the assumed isothermal conditions, if the diffusion flux follows Fick's law, then

$$J_j^{(\beta)} = -D_{\alpha\beta} \frac{\partial \rho_\beta}{\partial x_j}. \tag{26}$$

[J_j^β contains an external force term which does not contribute to eq. (24); also, for the particular system of carbon dioxide and water, the diffusion coefficient $D_{\alpha\beta}$ is assumed constant.] Also, for convenience we will define

$$C = \partial \mu_\beta / \partial \rho_\beta. \tag{27}$$

B. Variational Formulation

In accordance with Prigogine and Glansdorff,[12] eq. (23) is multiplied by $\delta(\mu_\alpha/T)$, eq. (24) by $\delta(\mu_\beta/T)$ and eq. (25) by $\delta v_i/T$, where μ_α and μ_β are the chemical potential per unit mass of the solvent and solute. For an isothermal system $(\delta \mu_\beta/T)$ can be written as

$$\frac{1}{T}\delta\mu_\beta = \frac{1}{T}\left[\tilde{V}_\beta \delta p + \frac{\partial \mu_\beta}{\partial \rho_\beta}\delta\rho_\beta + \frac{\partial \mu_\beta}{\partial \rho_\alpha}\delta\rho_\alpha\right]. \tag{28}$$

Since large pressure variations are required to give rise to changes in the chemical potential, the first term of eq. (28) is taken as zero. Also, for a dilute solute $\delta\rho_\alpha$ of the solvent vanishes. With these

assumptions and definitions, after some manipulation $\delta\phi$ becomes, corresponding to eq. (1),

$$\delta\phi = -\frac{1}{T}\int_V \Big[Cv_j \frac{\partial \rho_\beta}{\partial x_j}\,\delta\rho_\beta - CD\,\frac{\partial^2 \rho_\beta}{\partial x_j^2}\,\delta\rho_\beta + C\,\frac{\partial \rho_\beta^*}{\partial t}\,\delta\rho_\beta + \rho_0 v_j \frac{\partial v_i}{\partial x_j}\,\delta v_i + \frac{\partial p}{\partial x_j}\,\delta v_i - \mu\,\frac{\partial^2 v_i}{\partial x_j^2}\,\delta v_i - \rho_{\alpha_0} F_i^{(\alpha)}\delta v_i - \rho_\beta F_i^{(\beta)}\delta v_i + \rho_0 \frac{\partial v_i^*}{\partial t}\,\delta v_i \Big]\,dV. \tag{29}$$

Upon application of the divergence theorem, eq. (29) can be written as

$$T\delta\phi = -\int_V \Big[Cv_j \frac{\delta\rho_\beta}{\partial x_j}\,\delta\rho_\beta + C\,\frac{D}{2}\,\delta\left(\frac{\partial \rho_\beta}{\partial x_j}\right)^2 + C\,\frac{\partial \rho_\beta^*}{\partial t}\,\partial\rho_\beta + \rho_0 v_j \frac{\partial v_i}{\partial x_j}\,\delta v_i + \frac{\partial p}{\partial x_i}\,\delta v_i + \frac{\mu}{2}\,\delta\left(\frac{\partial v_i}{\partial x_j}\right)^2 - \rho_{\alpha_0} F_i^{(\alpha)}\delta v_i - \rho_\beta F_i^{(\beta)}\delta v_i + \rho_0 \frac{\partial v_i^*}{\partial t}\,\delta v_i \Big]\,dV - \int_S \Big[CD\,\frac{\partial \rho_\beta}{\partial x_j}\,\delta\rho_\beta + \mu\,\frac{\partial v_i}{\partial x_j}\,\partial v_i \Big] n_j\,dS. \tag{30}$$

Since the boundary conditions are time-independent, the surface integrals require as the natural boundary conditions on the bounding surfaces that the density and velocity remain constant. Thus, the surface integrals vanish.

Next

$$T\phi = \int_V \Big[C\rho_\beta v_j^*\,\frac{\partial \rho_\beta}{\partial x_j} + \frac{CD}{2}\left(\frac{\partial \rho_\beta}{\partial x_j}\right)^2 + \rho_0 v_j^* v_i\,\frac{\partial v_i^*}{\partial x_j} + \frac{\mu}{2}\left(\frac{\partial v_i}{\partial x_j}\right)^2 + v_i\,\frac{\partial p^*}{\partial x_i} - \rho_{\alpha_0}^* F_i^{(\alpha)*} v_i - \rho_\beta^* F_i^{(\beta)*} v_i + \rho_0 v_i \frac{\partial v_i^*}{\partial t} + C\rho_\beta \frac{\partial \rho_\beta}{\partial t} \Big]\,dV. \tag{31}$$

In accordance with eqs. (6) and (7), density, pressure, and

velocity perturbations are added to the terms describing flow in the stationary state

$$\begin{aligned} v_i &= v_i^s + \varepsilon u_i \, e^{-\sigma t} \\ \rho_\beta &= \rho_\beta^s + \varepsilon \gamma \, e^{-\sigma t} \\ p &= p^s + \varepsilon \eta \, e^{-\sigma t} \end{aligned} \tag{32}$$

where the superscript s denotes the steady state. The small parameter ε will be useful in subsequent ordering. The same functional forms are retained for the expected values

$$\begin{aligned} v_i^* &= v_i^s + \varepsilon \mu_i^* \, e^{-\sigma^* t} \\ \rho_\beta^* &= \rho_\beta^s + \varepsilon \gamma^* \, e^{-\sigma^* t} \\ p^* &= p^s + \varepsilon \eta^* \, e^{-\sigma^* t} \end{aligned} \tag{33}$$

Upon substitution of eqs. (32) and (33) into eqs. (31), $T\phi$ becomes

$$\begin{aligned} T\phi = \int_V \Bigg[& \varepsilon \, e^{-\sigma t} C \gamma v_j^s \frac{\partial \rho_\beta^s}{\partial x_j} + \varepsilon^2 \, e^{-(\sigma+\sigma^*)t} C \gamma u_j^* \frac{\partial \rho_\beta}{\partial x_j} \\ & + \varepsilon^2 \, e^{-(\sigma+\sigma^*)t} C \gamma v_j^s \frac{\partial \gamma^*}{\partial x_j} + \varepsilon \, e^{-\sigma t} C D \frac{\partial \rho_\beta^s}{\partial x_j} \frac{\partial \gamma}{\partial x_j} + \varepsilon^2 \, e^{-2\sigma t} C \frac{D}{2} \left(\frac{\partial \gamma}{\partial x_j} \right)^2 \\ & + \varepsilon \, e^{-\sigma t} \rho_0 v_j^s u_i \frac{\partial v_i^s}{\partial x_j} + \varepsilon^2 \, e^{-(\sigma+\sigma^*)t} \rho_0 u_j^* u_i \frac{\partial v_i^s}{\partial x_j} \\ & + \varepsilon^2 \, e^{-(\sigma+\sigma^*)t} \rho_0 v_j^s u_i \frac{\partial u_j^*}{\partial x_j} + \varepsilon \, e^{-\sigma t} u_i \frac{\partial p^*}{\partial x_i} + \varepsilon^2 \, e^{-(\sigma+\sigma^*)t} u_i \frac{\partial \eta^*}{\partial x_i} \\ & + \varepsilon \, e^{-\sigma t} \mu \frac{\partial v_i^s}{\partial x_j} \frac{\partial u_i}{\partial x_j} + \frac{\varepsilon^2 \, e^{-2\sigma t}}{2} \mu \left(\frac{\partial u_i}{\partial x_j} \right)^2 - \varepsilon \, e^{-\sigma t} \rho_{\alpha_0} u_i F_i^* \\ & - \varepsilon \, e^{-\sigma t} \rho_\beta^s u_i F_i^* - \varepsilon^2 \, e^{-(\sigma+\sigma^*)t} u_i \gamma^* F_i^* - \sigma^* \varepsilon^2 \, e^{-(\sigma+\sigma^*)t} \rho_0 u_i u_i^* \\ & - \sigma^* C \varepsilon^2 \, e^{-(\sigma+\sigma^*)t} \gamma \gamma^* \Bigg] \, dV. \end{aligned} \tag{34}$$

Terms that cannot be varied have been omitted in writing eq. (34) since they will vanish upon taking any variations. It should also be noted that third-order terms in ε have also been neglected, since the superposition principle is being used and is not applicable if third-order and higher terms are retained.

Equation (34) may be further reduced by specifying the relationships governing the stationary state. The coordinate system is

chosen so that x_3 is in the axial direction, x_2 is in the direction of the acceleration of gravity, and x_1 is orthogonal to both x_3 and x_2. The stationary-state velocity v_i^s is chosen so that only the axial velocity v_3^s is non-zero, *i.e.*, $v_1^s = v_2^s = 0$. The axial velocity v_1^s is assumed to be fully developed, that is, $v_3^s = v_3^s(x_1, x_2)$. For the particular case being considered, the only body force term will be that of gravity. Thus, $F_1 = F_3 = 0$ and $F_2 = \boldsymbol{g}$. It will also be assumed that the density distribution of the solute will be a function only of the vertical direction x_2, *i.e.*, $\rho_\beta^s = \rho_\beta^s(x_2)$. This is a limiting assumption since in the actual experimental apparatus the density was in principle a function not only of x_2 but also of x_1 and x_3. However, the effect of neglecting the gradient in the x_1 direction is small for small depths of penetration. The gradient of the density is also small in the axial direction x_3, and for short distances down the duct the density can be taken essentially as a constant. In other words,

$$\frac{\partial \rho_\beta^s}{\partial x_2} \gg \frac{\partial \rho_\beta^s}{\partial x_1} \qquad \frac{\partial \rho_\beta^s}{\partial x_2} \gg \frac{\partial \rho_\beta^s}{\partial x_3}.$$

Since the pressure gradient in the vertical direction can be expressed as

$$\frac{\partial p^s}{\partial x_2} = \boldsymbol{g}\,(\rho_\beta^s + \rho_{\alpha_0}) = \boldsymbol{g}\rho_0,$$

equation (34) becomes

$$\begin{aligned} T\phi = \int_V \Big[& \varepsilon^2 \, \mathrm{e}^{-(\sigma+\sigma^*)t} C\gamma u_2^* \frac{\mathrm{d}\rho_\beta^s}{\mathrm{d}x_2} + \varepsilon^2 \, \mathrm{e}^{-(\sigma+\sigma^*)t} C\beta v_3^s \cdot \frac{\partial \gamma^*}{\partial x_3} \\ & + \varepsilon \, \mathrm{e}^{-\sigma t} CD \frac{\mathrm{d}\rho_\beta^s}{\mathrm{d}x_2} \frac{\partial \gamma}{\partial x_2} + \varepsilon^2 \, \mathrm{e}^{-2\sigma t} \cdot \frac{CD}{2} \left(\frac{\partial \gamma}{\partial x_j} \right)^2 \\ & + \varepsilon^2 \, \mathrm{e}^{-(\sigma+\sigma^*)t} \rho_0 u_2^* u_3 \frac{\partial v_3^s}{\partial x_2} + \varepsilon^2 \, \mathrm{e}^{-(\sigma+\sigma^*)t} \rho_0 u_1^* u_3 \frac{\partial v_3^s}{\partial x_1} \\ & + \varepsilon^2 \, \mathrm{e}^{-(\sigma+\sigma^*)t} \rho_0 v_3^s u_1 \frac{\partial u_i^*}{\partial x_3} + \varepsilon \, \mathrm{e}^{-\sigma t} u_3 \frac{\partial p^s}{\partial x_3} + \varepsilon \, \mathrm{e}^{-\sigma t} \mu \frac{\partial v_3^s}{\partial x_2} \frac{\partial u_2}{\partial x_3} \\ & + \varepsilon^2 \, \mathrm{e}^{-2\sigma t} \cdot \frac{\mu}{2} \left(\frac{\partial u_i}{\partial x_j} \right)^2 - \varepsilon^2 \, \mathrm{e}^{-(\sigma+\sigma^*)t} u_2 \gamma^* \boldsymbol{g} \\ & - \sigma^* \varepsilon^2 \, \mathrm{e}^{-(\sigma+\sigma^*)t} (\rho_0 u_i u_i^* + C\gamma\gamma^*) \Big] \, \mathrm{d}V. \end{aligned} \tag{35}$$

It is seen that the pressure perturbation η does not appear in eq. (35).

The product of the velocity perturbation and the derivative of the pressure perturbation may be written as

$$\int_V u_i \frac{\partial \eta^*}{\partial x_i} \, dV = \int_V \left(\frac{\partial u_i \eta^*}{\partial x_i} - \eta^* \frac{\partial u_i}{\partial x_i} \right) dV.$$

The second term of this integral is zero because $\partial u_i / \partial x_i = 0$. When the divergence theorem is used, the first term may be written as

$$\int_V \frac{\partial u_i \eta^*}{\partial x_i} \, dV = \int_S \eta^* u_i \, . \, n_i \, dS$$

(where n_i is the surface normal), and is then zero because the normal component of the perturbation velocity at the boundary is assumed to be zero.

Equation (35) can now be integrated from 0 to θ, and equations equivalent to (9) and (10) formulated; these are not shown to save space.

Next the perturbations have to be expanded into suitable normal modes as indicated by eq. (16).

A general term of a Fourier expansion (which forms a complete set) is chosen for the arbitrary density perturbation

$$\gamma = \lambda(x_2) \cos \frac{k_1 x_1}{l_2} \cos \frac{k_3 x_3}{l_2}, \tag{36}$$

where λ is a function of x_2 only and $k^2 = k_1^2 + k_3^2$, where k is the wave number. It is also assumed that

$$u_2 = \xi(x_2) \cos \frac{k_1 x_1}{l_2} \cos \frac{k_3 x_3}{l_2}, \tag{37}$$

$$u_1 = \frac{-l_2 k_1}{k^2} \frac{d\xi}{dx_2} \sin \frac{k_1 x_1}{l_2} \cos \frac{k_3 x_3}{l_2}, \tag{38}$$

$$u_3 = \frac{-l_3 k_3}{k^2} \frac{d\xi}{dx_2} \cos \frac{k_1 x_1}{l_2} \sin \frac{k_3 x_3}{l_2}, \tag{39}$$

where ξ is a function of x_2. These are the forms for rectangular cells with l_1 and l_3 chosen so that

$$\sin \frac{k_1 l_1}{l_2} = \sin \frac{k_3 l_3}{l_2} = 0.$$

The functional forms of the velocities have been selected so that the continuity equation is also satisfied, that is,

$$\frac{\partial u_i}{\partial x_i} = 0.$$

Substituting eqs. (36) through (39) into the equation for p_1 and performing the integrations over x_1 and x_3 gives

$$p_1 = \varepsilon^2 \frac{l_1 l_3}{4} \int_0^{l_2} \left\{ \lambda \xi^* C \frac{\mathrm{d}\rho_\beta^s}{\mathrm{d}x_2} - g\lambda^* \xi - \sigma^* \left(\frac{l_2^2 \rho_0}{k^2} \frac{\mathrm{d}\xi}{\mathrm{d}x_2} \frac{\mathrm{d}\xi^*}{\mathrm{d}x_2} + \rho_0 \xi \xi^* + C \lambda \lambda^* \right) \right\} \mathrm{d}x_2 + \varepsilon^2 \frac{l_1 l_3}{4} \int_0^{l_2} \left\{ \frac{CD}{2} \left[\frac{k^2}{l_2^2} \lambda^2 + \left(\frac{\mathrm{d}\lambda}{\mathrm{d}x_2} \right)^2 \right] + \frac{\mu}{2} \left[2 \left(\frac{\mathrm{d}\xi}{\mathrm{d}x_2} \right)^2 + \frac{k^2}{l_2^2} \xi^2 + \frac{l_2}{k^2} \left(\frac{\mathrm{d}^2 \xi}{\mathrm{d}x_2^2} \right)^2 \right] \right\} \mathrm{d}x_2. \tag{40}$$

It is seen that all first-order terms in ε and terms involving the axial velocity v_3^s have vanished.

The variation of p_1 with respect to λ and ξ may now be taken, as called for by eq. (13), and the resulting expression may be equated to zero and solved for λ and ξ. However, this leads to two simultaneous coupled non-linear differential equations which prove difficult to solve. The alternate procedure of solution is used here which involves choosing the functional forms of λ and ξ in x_2, performing the indicated integrations over x_2, and then taking the variation of p_1 as indicated by eq. (19). The variation is then set equal to zero, to yield a relationship between the stability parameter σ and the physical properties and dimensions of the system as indicated by eq. (20).

Several forms for the steady-state density gradient have been studied. Three will be presented here. In particular, a linear density-gradient form will be examined first, and subsequently the analysis will cover two non-linear density forms, namely, those given by the solution to the modified penetration theory and by a boundary-layer analysis.

C. Case I: Linear Steady-state Density Distribution

For illustrative purposes, the calculations based on an assumed linear density gradient are presented first, although such a gradient

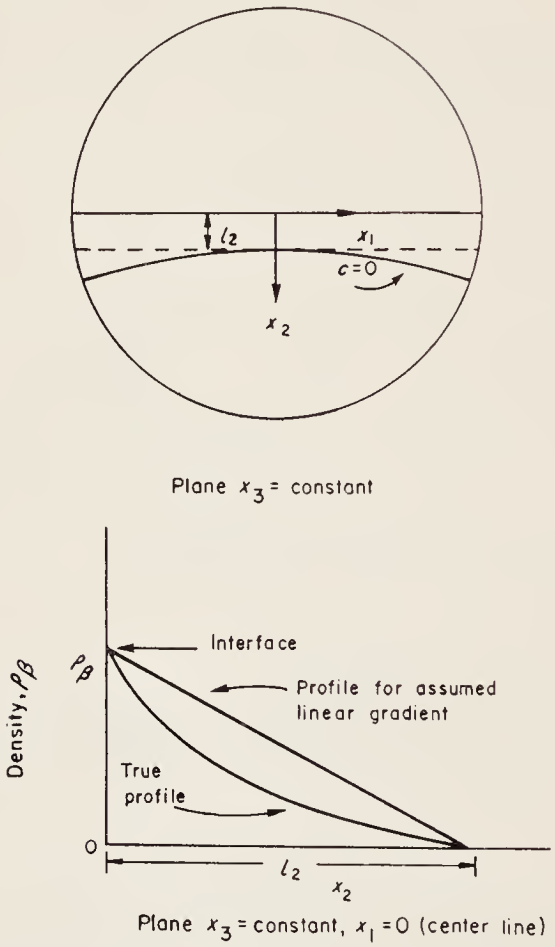

Fig. 1. Density profiles for actual and hypothetical physical systems.

does not truly represent the physical system used in the experimental work. For case I

$$\frac{d\rho_\beta^s}{dx_2} = -\omega,$$

where ρ_β^s is the steady-state concentration of component β expressed in terms of mass per unit volume. The steady-state density profile

of the hypothetical system is shown in Fig. 1, along with the true profile. Because of the similarity of heat and mass transfer, the problem posed is an analog of the Bénard problem. A type of modified critical Rayleigh number is found, which involves mass-transfer terms rather than heat-transfer terms.

It now remains to choose the forms for λ and ξ. The choice is not arbitrary since λ and ξ have to satisfy the boundary conditions

$$\xi = \frac{\mathrm{d}\xi}{\mathrm{d}x_2} = 0 \quad \text{for} \quad x_2 = 0 \quad \text{and} \quad l_2$$

and

$$\lambda = 0 \quad \text{for} \quad x_2 = 0 \quad \text{and} \quad l_2. \tag{41}$$

As an approximation it was assumed that

$$\xi = A\left(1 - \frac{x_2}{l_2}\right)^2\left(\frac{x_2}{l_2}\right)^2 \tag{42}$$

and

$$\lambda = E\left(1 - \frac{x_2}{l_2}\right)\left(\frac{x_2}{l_2}\right). \tag{43}$$

Substitution of eqs. (41), (42), and (43) into eq. (40) yields, after integration over x_2,

$$p_1 = \varepsilon^2 \frac{l_1 l_3}{4}\left[-\frac{CEA^*\omega l_2}{140} - \frac{9E^*Al_2}{140} - \frac{\sigma^*\rho_0 l_2}{k^2}\cdot\frac{2AA^*}{105}\cdot\frac{\sigma^*\rho_0 l_2 AA^*}{630} - \frac{\sigma^*CEE^*l_2}{30}\right] + \varepsilon^2\frac{l_1 l_3}{4}\left[\frac{CDk^2E^2}{60l_2} + \frac{CDE^2}{6l_2} + \frac{2\mu A^2}{105l_2} + \frac{\mu k^2A^2}{1260l_2} + \frac{2\mu A^2}{5k^2l_2}\right]. \tag{44}$$

Next, to take the variations of p_1, the constants A and E have to satisfy the following relations

$$\delta p_1/\delta A = 0 \tag{45a}$$

and

$$\delta p_1/\delta E = 0 \tag{45b}$$

as well as subsequently the auxiliary conditions $A = A^*$, $E = E^*$, and $\sigma = \sigma^*$. Equation (45a) leads to

$$\left[\frac{4}{5k^2} + \frac{4}{105} + \frac{k^2}{630} - \frac{2\Phi}{105k^2} - \frac{\Phi}{630}\right] A - \left[\frac{gl_2^2}{140\mu}\right] E = 0; \quad (46)$$

while eq. (45b) gives

$$\left[\frac{-l_2^2\omega}{140D}\right] A + \left[\frac{1}{3} + \frac{k^2}{30} - \frac{\Phi Sc}{30}\right] E = 0, \quad (47)$$

where $Sc = \dfrac{\mu}{\rho_0 D}$ = Schmidt number

and $\Phi = \dfrac{\sigma l_2^4 \omega}{\mu D}$ = dimensionless decay rate.

Thus, two linear, homogeneous simultaneous algebraic equations are obtained which have the solution, when the determinant of the coefficient matrix vanishes, of

$$R = (140)^2 \left[\frac{4}{5k^2} + \frac{4}{105} + \frac{k^2}{630} - \frac{2\Phi}{105k^2} - \frac{\Phi}{630}\right]\left[\frac{1}{3} + \frac{k^2}{30} - \frac{\Phi Sc}{30}\right], \quad (48)$$

where $R = \dfrac{gl_2^4\omega}{\mu D}$ = modified Rayleigh number.

Equation (48) gives the relationship between the modified Rayleigh, Schmidt, and wave numbers, and the decay rate. If the decay rate has a negative real part, the system will be unstable.

One of the principal objects of an investigation of hydrodynamic stability is the determination of the state of marginal stability, *i.e.*, the locus which separates the stable from the unstable state and is given by $\Phi = 0$ (see Fig. 2). Introduction of $\Phi = 0$ into eq. (48) gives the relationship between the modified Rayleigh number and the wave numbers for marginal stability. For a particular critical wave number (k_c) a critical modified Rayleigh number (R_c) is obtained, which is the largest modified Rayleigh number for which the system can remain stable for all wave numbers. If Φ is equated to zero in eq. (48), and the derivative dR/dk is equated to zero, the critical wave number is obtained: $k_c = 3.117$. If this value is inserted into eq. (48) with $\Phi = 0$,

the critical modified Rayleigh number R_c is found to be 1,740. Since case I corresponds to the Bénard problem, for which the exact solution[3] is $k_c = 3.117$ and $R_c = 1{,}708$, the approximate results compare favorably.

The only stipulation for the choice of the forms for ξ and λ was that they were to satisfy the boundary conditions given by eq. (41).

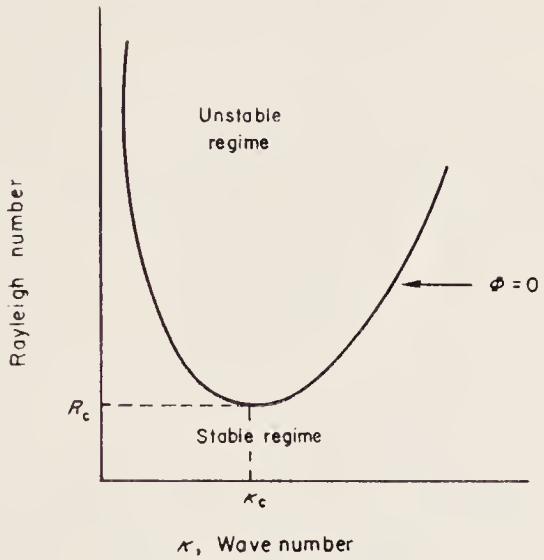

Fig. 2. Marginal stability.

Other forms for ξ and λ have been investigated; for example, ξ and λ were taken to be

$$\xi = A \sin^2 \frac{\pi x_2}{l_2} \tag{49}$$

and

$$\lambda = E \sin \frac{\pi x_2}{l_2}. \tag{50}$$

[Note that these forms also satisfy the boundary conditions (41).] By following the procedure described above it was found that the critical wave number was $k_c = 3.117$, and the corresponding critical modified Rayleigh number was $R_c = 1{,}824$.

To see if the approximate solutions, eqs. (42) and (43), could be

improved by a larger number of adjustable constants, eq. (42) was expanded by one more term

$$\xi = A\left(1 - \frac{x_2}{l_2}\right)^2\left(\frac{x_2}{l_2}\right)^2 + B\left(1 - \frac{x_2}{l_2}\right)^3\left(\frac{x_2}{l_2}\right)^3, \tag{51}$$

and eq. (43) also by one more term

$$\lambda = E\left(1 - \frac{x_2}{l_2}\right)\left(\frac{x_2}{l_2}\right) + F\left(1 - \frac{x_2}{l_2}\right)^2\left(\frac{x_2}{l_2}\right)^2. \tag{52}$$

Again note that the chosen forms satisfy the boundary conditions (41). Since there were now four free constants, the following variations had to be taken after the integrations:

$$\begin{aligned} \delta p_1/\delta A &= 0 \\ \delta p_1/\delta B &= 0 \\ \delta p_1/\delta E &= 0 \\ \delta p_1/\delta F &= 0 \end{aligned} \tag{53}$$

For the boundary conditions (41), eqs. (53) lead to four linear, simultaneous algebraic equations and hence to a characteristic equation evolving from a fourth-order determinant. Solution of this characteristic equation for the case of marginal stability gave a critical modified Rayleigh number of $R_c = 1{,}731$ and a corresponding critical wave number $k_c = 3.117$. Thus, it is seen that the expansions (51) and (52) represent little improvement over (42) and (43).

Case I describes for mass transfer a hypothetical physical situation which cannot be fulfilled in reality, and the conditions for marginal stability predicted in this Section have validity only when compared with the Bénard problem which is a direct analogy in heat transfer.

D. Case II: Complementary Error Function as the Steady-state Density Distribution

As previously mentioned, the linear gradient is not a truly representative choice for gas absorption. The procedure employed above will now be extended to include a non-linear density gradient that has been selected to be that given by the solution

of the modified penetration theory for co-current stratified flow in a half-filled round tube[1]

$$\rho_\beta^s = \rho_{\beta_i} \operatorname{erfc} \left[\frac{x_2}{2} \sqrt{\frac{K\bar{w}_L(1 - x_1^2/R_t^2)}{Dx_3}} \right], \tag{54}$$

where

$$\rho_{\beta_i} = \text{density of solute at } x_2 = 0$$

and where the relation

$$\rho_\beta = c_\beta M_\beta$$

has been used. It is seen that the density given by eq. (54) is a function of all three coordinates x_1, x_2, and x_3. However, the assumption $\rho_\beta^s = \rho_\beta^s(x_2)$ is a good approximation across most of the duct, except very near the walls. Thus, evaluating eq. (54) at the center line $x_1 = 0$ yields

$$\rho_\beta^s = \rho_{\beta_i} \operatorname{erfc} \frac{x_2}{2} \sqrt{\frac{K\bar{w}_L}{Dx_3}} \tag{55}$$

By use of the relation

$$w_{i_c} = K\bar{w}_L$$

an arbitrary diffusion length $l_2^{(4)}$ (see Fig. 3) can be defined

$$l_2 = 2a \sqrt{\frac{Dx_3}{w_{i_c}}} = 2a\sqrt{Dt}. \tag{56}$$

The constant a depends on the definition of the diffusion length l_2. For example, if the diffusion length is defined as that length at which the concentration is one-hundredth of that at the interface, then $a = 1.822$. Equation (55) now reduces to

$$\rho_\beta^s = \rho_{\beta_i} \operatorname{erfc} a \left(\frac{x_2}{l_2} \right), \tag{57}$$

where t is taken as the contact time of an element of fluid traveling along the gas–liquid interface at $x_1 = 0$. It should be noted that l_2 increases down the length of the duct, but for short duct lengths

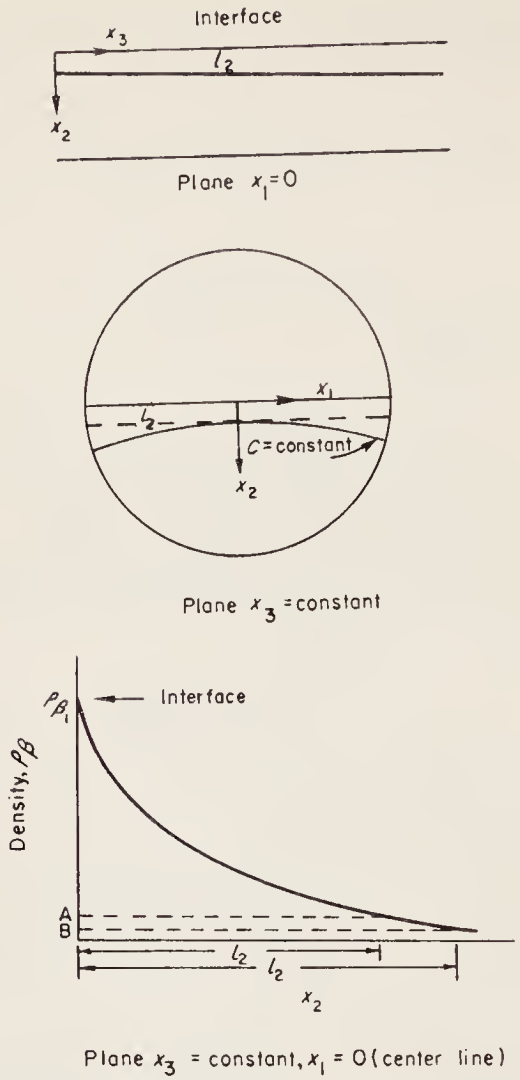

Fig. 3. Density profiles.

l_2 can be treated as essentially a constant. Differentiation of eq. (57) yields for the density gradient

$$\frac{d\rho_\beta^s}{dx_2} = \frac{-2a\rho_{\beta_i}}{\sqrt{\pi} \cdot l_2} \exp\left[-a^{2(x_2/l_2)^2}\right]. \tag{58}$$

Since the boundary conditions for the density and velocity perturbations remain the same as given by eq. (41), the same

forms for λ and ξ will be chosen, namely, those given by eqs. (42) and (43). Thus, the only new integral that needs to be evaluated in eq. (40) is the first, *i.e.*,

$$I_1 = \int_0^{l_2} C\lambda\xi^* \cdot \frac{\mathrm{d}\rho_\beta^s}{\mathrm{d}x_2}\,\mathrm{d}x_2. \tag{59}$$

After substitution of eqs. (42), (43), and (57) into eq. (59), and repeated integration by parts, it is found that

$$I_1 = -\frac{CEA^*\rho_{\beta_i}}{\sqrt{\pi}}\left[\frac{-9a\,\mathrm{e}^{-a^2} + 4a^3 - 13.4394a^2 + 24a - 11.1194}{4a^6}\right] \tag{59a}$$

where I_1 now replaces the first term in eq. (44).

By following the same procedure as in case I, it was found that

$$R = (140)\left[\frac{4\sqrt{\pi}\cdot a^6}{-9a\,\mathrm{e}^{-a^2} + 4a^3 - 13.4394a^2 + 24a - 11.1994}\right] \times \left[\frac{4}{5k^2} + \frac{4}{105} + \frac{k^2}{630} - \frac{2\Phi}{105k^2} - \frac{\Phi}{630}\right]\left[\frac{1}{3} + \frac{k^2}{30} - \frac{\Phi Sc}{30}\right], \tag{60}$$

where the previous modified Rayleigh number definition has been redefined so that now

$$R = \frac{g l_2^3 \rho_{\beta_i}}{\mu D}.$$

For the case of marginal stability ($\Phi = 0$), the critical wave number k_c is found to be 3.117 as before. The critical modified Rayleigh number is a function of the constant a:

$$R_c = \frac{87.7707a^6}{-9a\,\mathrm{e}^{-a^2} + 4a^3 - 13.4394a^2 + 24a - 11.1994}.$$

To calculate the value of a it is necessary to define a diffusion length l_2 for a particular contact time t as given by eq. (56).

E. Case III: Steady-state Distribution Derived from a Boundary-layer Analysis

An obvious disadvantage of using the complementary error function profile given by eq. (57) is that it requires a choice of a diffusion length l_2 in order to evaluate the constant a. However,

as shown in Section II of reference 1 by a boundary-layer analysis, a polynomial representation can be used to approximate the steady-state density distribution, and the polynomial has the advantage that an arbitrary diffusion length l_2 does not have to be specified. Thus, case III represents the distribution by

$$\frac{\rho_{\beta_i} - \rho_\beta^s}{\rho_{\beta_i}} = 2\left(\frac{x_2}{\delta_c}\right) - 2\left(\frac{x_2}{\delta_c}\right)^3 + \left(\frac{x_2}{\delta_c}\right)^4, \tag{61}$$

where δ_c is the diffusion boundary layer thickness. The density gradient is then given by

$$\frac{d\rho_\beta^s}{dx_2} = -\frac{\rho_{\beta_i}}{\delta_c}\left[2 - 6\left(\frac{x_2}{\delta_c}\right)^2 + 4\left(\frac{x_2}{\delta_c}\right)^3\right]. \tag{62}$$

If, as before, the density and velocity perturbations are given by eqs. (42) and (43), the only new integral that needs to be evaluated in eq. (40) is the first, *i.e.*,

$$I_1 = \int_0^{\delta_c} C\lambda\xi^* \frac{d\rho_\beta^s}{dx_2}\, dx_2,$$

where the integration over x_2 is from $x_2 = 0$ to $x_2 = \delta_c$ rather than from 0 to l_2 as previously. This integration leads to

$$I_1 = \frac{CEA^*\rho_{\beta_i}}{140},$$

which is the same result as in the case for a linear density gradient or

$$R_c = \frac{g\delta_c^3\rho_{\beta_i}}{\mu D} = 1{,}740 \tag{63}$$

for $k_c = 3.117$. For further investigation, a four-constant density distribution for ρ_β^s was assumed which still satisfied the boundary conditions employed in the boundary-layer analysis. It was found that

$$\frac{\rho_{\beta_i} - \rho_\beta^s}{\rho_{\beta_i}} = \frac{1}{2}\left[3\left(\frac{x_2}{\delta_c}\right) - \left(\frac{x_2}{\delta_c}\right)^3\right],$$

so that

$$\frac{d\rho_\beta^s}{dx_2} = -\frac{\rho_{\beta_i}}{2\delta_c}\left[3 - 3\left(\frac{x_2}{\delta_c}\right)^2\right]. \tag{64}$$

When the previous procedure was followed, the critical modified Rayleigh number was $R_c = 1606$ for $k_c = 3.117$.

Various other hypotheses were examined as to the steady-state density distribution and the functional forms of ξ and λ. Results of these analyses are too detailed to present here but are given in ref. 1.

F. Stability Parameter

The equation for σ, eq. (15), does not directly establish the stability in the case of gas absorption, because the sign of the numerator can be evaluated only after eq. (13), *i.e.*, here eq. (19), has been applied. Since the results of eq. (19), such as eqs. (45) and (46), themselves relate the stability parameter to the physical variables for the problem considered, there has been no need to work out eq. (15) separately.

IV. COMPARISON OF THEORY WITH EXPERIMENT

To test the predictions of marginal stability derived in Section III for a flowing fluid, the experimental conditions should agree with the mathematical model as closely as possible. However, some compromises are necessary. Optical techniques,[11] which are satisfactory in static systems, are inconvenient to use for a flowing system. Instead, Ball[1] detected instability effects for the postulated experiment of gas absorption by measuring the increase in exit concentration of carbon dioxide in water in a stratified duct over that predicted for a stable system. The gas-absorption measurements were made in a horizontal, glass, circular cylinder duct of 3″ internal diameter, with a calming section 2 feet long, a transfer section 8 feet long, and a short exit section.

In order to predict with accuracy the average exit concentration of gas, $\bar{c}_L$, it was necessary to know the steady-state interfacial liquid velocity across the duct, and to account for the entrance velocity effects on the exit gas concentration, which might be mistaken for stability effects. With the aid of the work of Semenov and Tochigin,[15] dimensionless velocity expressions were developed

for both the gas and the liquid phase for the particular case of a duct half-filled with water and half-filled with carbon dioxide. Interfacial velocities were measured and compared with the predicted velocity expressions. The entrance region proved to be quite long, even for the lowest flow rates, hence the exit concentrations calculated without including the effect of the entrance region had to be corrected.

The interface of the duct was divided into sections 1 inch long and 0.125 inch wide. The experimentally determined entrance-region interfacial velocities were used; the average interfacial velocities for each of these small sections were determined, and the interphase mass-transfer contributions from each of these sections as predicted by the well-known penetration theory of Danckwerts[4] were then summed across and down the duct to determine the total amount of carbon dioxide transferred. (A boundary-layer analysis predicted exit concentrations which agreed within 3% with those of the penetration theory.) The concentrations determined by ignoring the entrance region are compared in Table 1 with those determined by including the effect

TABLE 1. Average Liquid Exit Concentration Based on the Modified Penetration Theory

Average liquid velocity, $\bar{w}_L$ (in/sec)	Exit concentrations (mg CO_2/100 ml)		Difference (%)
	without adjustment for entrance region	with adjustment for entrance region	
0.050	13.59	—	—
0.075	11.08	11.71	5.7
0.100	9.61	10.18	5.9
0.125	8.59	9.34	8.7
0.150	7.85	8.78	11.8
0.200	6.79	7.67	13.0
0.240	6.20	7.17	15.6
0.267	5.88	6.91	17.5

of the entrance region. Fig. 4 shows a comparison of the predicted and the experimental average outlet concentrations found in this

work. Considerable difference can be noted. After detailed examination of possible pertinent factors, the difference was ascribed to augmented liquid mixing engendered by instability.

Because accurate experimental measurements of the very dilute exit-gas concentrations could be made only in a certain range of flow rates, the physical conditions in the duct corresponded

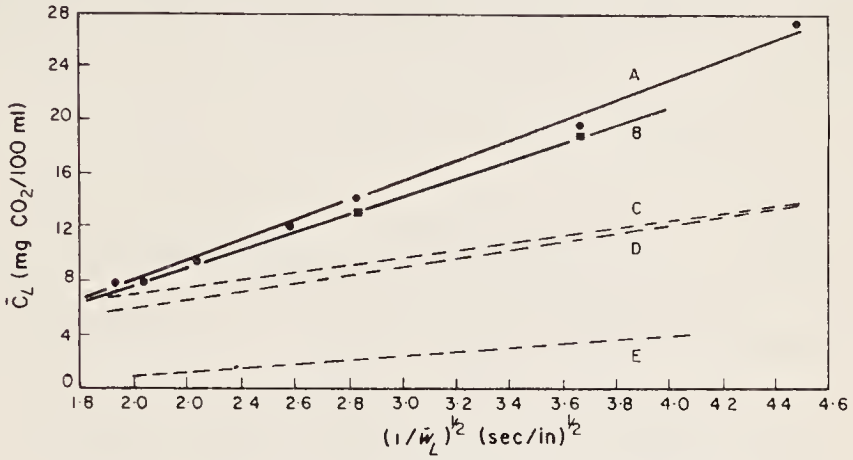

Fig. 4. Average exit concentration plotted against measure of flow rate.

A, Experimental, without interfacial monolayer.
B, Experimental, with interfacial monolayer.
C, Modified penetration theory with entrance length adjustment.
D, Modified pentration theory without entrance region adjustment.
E, Theory, with interfacial monolayer.

to the unstable regime illustrated schematically in Fig. 2. Inasmuch as the Rayleigh numbers developed in Section III were for the *onset* of instability at any wave number—predictions of flow and concentration for the unstable region would require solution of eqs. (20)—the experimental measurements had to be extrapolated slightly from the unstable region to a "point" of stability; refer to Fig. 5.

The extrapolation was carried out as follows. For each experimental run with known average liquid velocity a modified Nusselt number for mass transfer was calculated by forming the ratio of

the experimental average exit concentration and the concentration predicted by the penetration theory including the effect of the entrance length. The modified Nusselt number so formed represents the ratio of the carbon dioxide actually transported across the interface to that which would be transported by diffusion alone (no instability) as predicted by the penetration theory. A value of the modified Nusselt number greater than one indicated enhanced interphase mass transfer, presumably caused by instability.

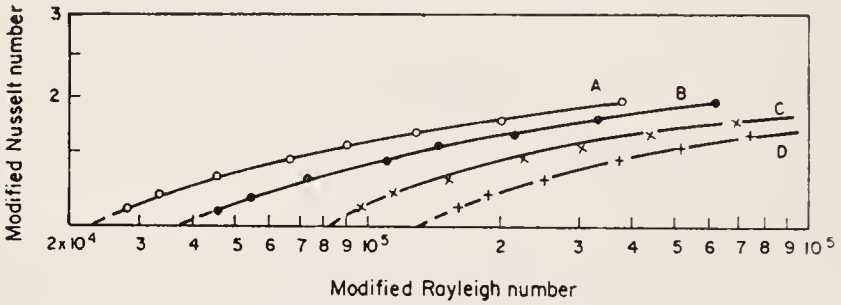

Fig. 5. Modified Nusselt number plotted against modified Rayleigh number.

A, Boundary layer theory.
B, $a = 1.822$.
C, $a = 2.327$.
D, $a = 2.752$.

A modified Rayleigh number, as defined in Section III, was calculated for each modified Nusselt number. For example, for the boundary-layer analysis of case III, by making use of definition (63) plus the definition of the diffusion-layer thickness δ_c, namely,

$$\delta_c = 0.159 \left[\bar{w}_L \left(1 - \frac{x^2}{R^2} \right) \right]^{-1/2}, \tag{65}$$

the modified Rayleigh number could be related to the average duct velocity and the position at the interface. For case II, the diffusion depth l_2 was given by eq. (56) and introduced into

$$R = \frac{g l_2^3 \rho_{\beta_i}}{\mu D},$$

a becoming a parameter.

A plot was next prepared of the modified Nusselt number *versus* the modified Rayleigh number, and the curve of best fit was extrapolated to a modified Nusselt number of unity as indicated by the dashed lines of Fig. 5, which is for $x = 0$, *i.e.*, the center line. The modified Rayleigh number corresponding to the modified Nusselt number of unity was termed the "pseudo-critical modified Rayleigh number", and in effect represents the point at which the average liquid exit concentration would be just equal to that predicted by the penetration theory.

Table 2 provides a comparison of the predicted critical Rayleigh

TABLE 2. Comparison of Rayleigh Numbers

Case	Steady-state density distribution ρ	Predicted critical Rayleigh number			Experimental Rayleigh number*
I	$-\omega x_2$	1,731–1,740			
		c/c_i	a	R_c	
II	$\rho_{\beta i}$ erf $c[a(x_2/l_2)]$	10^{-2}	1.822	742	3.8×10^4
		10^{-4}	2.752	1,743	1.4×10^5
III	$-\rho_{\beta i}[(2x_2/\delta_c) - 2(x^2/\delta_c)^2 + (x_2/\delta_c)^4]$ and variations	1,606–1,740			2.4×10^4

* Based on the center-line velocity.

numbers with the measured pseudo-critical numbers. In case II, a diffusion length l_2 must be defined in terms of the "penetration depth" for diffusion, *i.e.*, the depth at which the concentration c is a certain fraction of the interfacial concentration c_i. Among the various steady-state density-distribution models and diffusion lengths considered here and in ref. 1, probably the most realistic is that based on the boundary-layer theory (case III) since this model is independent of an arbitrary definition of the diffusion length l_2. For this case, the predicted critical Rayleigh number was about 7% of the pseudo-critical Rayleigh number. The modified penetration-theory steady-state density-distribution model (case II) will be ignored because it requires an arbitrary definition of a diffusion depth in order to calculate the value l_2.

Case I will also be neglected because the steady-state density profile in the experimental apparatus was certainly not linear.

In view of the simplifications that have been made in the mathematical model, and the differences between the simplified model and the experiment, the discrepancies between the predicted and the measured Rayleigh number is not unexpected. Keep in mind that the predicted values of R_c represent lower bounds and are indeed less than the measured pseudo-critical values. In the derivation of the critical modified Rayeligh number, it was assumed that the cell patterns were rectangular. This assumption is sound in the theorethical analysis since the critical modified Rayleigh number is independent of the cell shape and size. As Chandrasekhar[3] points out, the walls of the cell are surfaces of symmetry that are vertical, and the normal gradient of the vertical velocity vanishes on the cell walls. In the theoretical analysis the velocity distribution does not appear in the determination of the stability criterion because unit cells were assumed, and the terms arising from the velocity gradients became zero after the integrations over x_1 and x_2. However, since there were velocity variations in both the x_1 and the x_2 direction in the liquid phase of the experimental circular duct, they would, if rectangular cells were formed, not long retain their identity because of velocity gradients, although these velocity gradients within the diffusion layer are small. The shape of the distorted cells in the physical case would be exceedingly difficult to determine and involve an immense mathematical problem. Thus, theoretical models that were not strictly realizable physically have been considered in the stability analysis. These simplified models were chosen because the exact mathematical problem was so formidable that simplifications were necessary for solution. However, the simplified theory can lay the groundwork for handling more complete and complicated models.

A second factor which helps to explain the difference between observed and predicted Rayleigh numbers is that the denominator of the modified Nusselt number was based on a varying interfacial velocity across the duct to correspond with the actual velocity field instead of being based on a uniform velocity. If the experimental apparatus had actually operated in plug flow in the liquid phase, less mass transfer would have occurred,

and the values of the modified Nusselt numbers plotted in Fig. 5 would have been displaced upward. With this adjustment, re-extrapolation of the curves would give lower critical modified Rayleigh numbers. Thus, the theoretical and experimental numbers would agree more closely.

The results of Tang and Himmelblau[22] mentioned previously, which did not note any effect of instability, were obtained for flow rates an order of magnitude higher than those used in the experimental part of this study. In Fig. 4 these flow rates would appear considerably to the left of the first abscissa index value, and can be seen to fall in the region where instability has little noticeable influence.

It is concluded that the large deviations between the experimentally determined exit concentrations and those predicted by theory could not be explained by entrance effects, and also not by errors in the experimental procedure or in the mathematical model for diffusion. Instead, it is felt that these deviations were caused by mixing engendered by instability in the liquid phase, especially since theoretical analysis showed qualitatively that instability could develop. Density-generated instability in gas absorption can enhance interphase transfer only when the interface is horizontal and the exposure times are relatively long.

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LOCAL POTENTIAL METHODS IN THE STUDY OF KINETIC EQUATIONS*

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1. INTRODUCTION

1.1. Variational Principles in Continuum Physics

In problems of macroscopic physics as well as in statistical mechanics one is often interested in calculating solutions of the general equations of evolution that are steady or slowly vary in time, and it has long been realized that in most cases such solutions provide a satisfactory description of a given physical situation. A question which is less evident, but which nevertheless should arise whenever one solves such problems, is under what conditions such solutions are physically admissible, i.e. under

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what conditions they represent stable solutions[1] to the equations of evolution.

In classical thermodynamics this dual aspect of steady states was realized very clearly and it was clarified in a completely satisfactory way. Indeed, it was shown that there exist functions, such as entropy and free energy, which depend on the thermodynamic variables and assume extremal values at equilibrium.[2] Such properties of the above quantities, known as thermodynamic potentials, were sufficient when building the whole theory of equilibrium thermodynamics and when investigating the stability of equilibrium configurations. They were extended to the linear and the non-linear domain of non-equilibrium thermodynamics some time ago.[3] Very recently it was also possible to generalize further and incorporate the study of both convective and dissipative processes in a single formalism. In all these generalizations the central point was to find new potentials whose extremum properties could assume the stability of the steady solutions of the macroscopic equations, which in the case of non-equilibrium thermodynamics with convective processes were just the three well-known equations of conservation of mass, of momentum, and of energy, supplemented by the Gibbs assumption about the definition of entropy.[3] While the entropy production turned out to be such a potential in the linear domain of thermodynamics, it was recently realized that in more general situations the concept of thermodynamic potential should be drastically modified in order to cover both non-linear thermal and convective process. It was this remark that led to the local potential recently introduced by Prigogine and Glansdorff.[4] At the same time, it was possible to show that this same local potential could generate the conservation equations by means of a well-defined variational procedure.[4,5]

Variational principles have long been used in the study of many physical problems. Besides the well-known principles used in classical and in quantum mechanics, many problems giving rise to self-adjoint linear differential equations were studied by means of the well-known Rayleigh–Ritz method or of one of its modifications.[6] It was possible to construct "Lagrangian", functionals of the unknown quantities giving rise to the equations of evolution in the usual sense of the calculus of variations: If

$$L = \int_D \mathscr{L}(f)\, \mathrm{d}V, \tag{1.1a}$$

then

$$\delta L/\delta f = 0 \tag{1.1b}$$

gives rise to the well-known Euler–Lagrange equations which are precisely the equations of the problem under consideration in the domain D. Moreover, the functional L has a minimum for the solution $\bar{f}$ of eq. (1.1b). It is therefore automatically established that the solution $\bar{f}$ is stable and that it is possible to construct approximate solutions of eq. (1.1b) converging to the true solution.

It was a problem of obvious importance to extend these variational techniques to more general situations described by non-self-adjoint or non-linear equations, as for example, to the study of hydrodynamic and hydromagnetic problems. Unfortunately, although it was possible to construct quantities L satisfying eq. (1.1b), it proved impossible to assure extremal properties for them, except in a few particular cases. Yet such variational principles met with considerable success in studies of many problems, even though the lack of proof of any convergence property had to be overcome by a judicious choice of trial functions (see refs. 7–9 for typical examples).

Under those circumstances the step achieved by the introduction of the Prigogine–Glansdorff variational principle of local potential[4,5] is especially important. Indeed, this local potential exhibits a minimum property (to be explained below) and may lead, moreover, to convergent sequences of approximate solutions.[10,11] It should, therefore, be possible to formulate both steady-state and stability problems in terms of this potential and a number of steps in this direction has already been carried out.[12,13]

On the other hand it is fair to note that a large class of non-self-adjoint problems can be studied by other methods not necessarily associated with variational principles. Among these, we especially notice Galerkin's method,[6,14,15] which however has mainly been applied to the study of linear equations. Finally we should remember that the stability of solutions of a large class of systems of equations, both linear and non-linear, but

mainly ordinary differential and integro-differential, is very conveniently studied by means of the Lyapounoff methods.[1,16]

1.2. Variational Methods for the Study of Kinetic Equations in Statistical Mechanics

The problems of determining quasi-steady-state solutions of the kinetic equations and of studying their stability properties also constitute a central problem in statistical mechanics and in kinetic theory. Again, variational techniques were very soon found to be quite essential, both for the practical reason for solving the Boltzmann equation and for their connexion to the macroscopic properties of the system. Indeed, for the study of the Boltzmann equation linearized about local equilibrium, it turned out that the Lagrangian giving rise to the equation as well as to a minimum property was very closely related to the entropy production.[17,18] It was, moreover, realized that once one passes to non-self-adjoint problems the extremal property disappears, unless one artificially modifies the problem by introducing an additional evolution operator whose properties may assure the existence of extremal solutions.[18,19] In any case, non-self-adjoint kinetic equations without extremal Lagrangians have also been studied in several examples with reasonably good results.[8,9,18,19]

It is the purpose of the present study to propose a variational method for non-self-adjoint and/or non-linear kinetic equations which permits a connexion with the thermodynamic and the stability properties of the system. The extremal property of this variational technique, which largely provides it with its physical content, is, however, to be formulated, not in the usual sense,[17] but in the sense of fluctuation theory, as it will be explained below.

The ideas included in the construction of the local potential by Prigogine and Glansdorff[4,5,11] already made it possible to construct such a variational principle for continuum systems. We shall prove that they can be extended to the study of kinetic equations[20] with similar advantages, allowing a unified description of several properties of these equations. We shall first construct, in section 2, the local potential for a typical form of a kinetic equation and comment on its properties. Next we shall compare,

in section 3, the variational technique associated with this potential and other approaches to a study of the properties of the kinetic equations. We shall also discuss the problem of convergence of approximate solutions, constructed on the basis of the local potential, to the exact solution. In section 4, we shall restrict our field of interest and discuss the application of the local potential to the study of stability of the solutions of the kinetic equations. Section 5 will be devoted to an application of the analysis given in section 4 to a specific problem. Finally, in section 6, we shall present a discussion and an outline of the domain of applicability of local-potential methods.

Before proceeding to our detailed analysis, we notice that, just as in the case under sub-section 1.1, one could consider a possible application of Galerkin's and Lyapounoff's techniques to the study of kinetic equations. Some remarks regarding this question will be given in Sections 3 and 4.

2. THE LOCAL POTENTIAL

We consider a system of many particles characterized by their instantaneous positions and velocities and we assume periodic boundary conditions. To illustrate our calculations, we shall always limit ourselves to systems which are dilute enough for encounters between particles to be considered as instantaneous and localized events. This implies, of course, that we shall have to consider only slowly varying external constrains. Such systems are completely characterized by their one-particle Boltzmann distribution function $f(\mathbf{x}, \mathbf{v}, t)$, defined in molecular coordinate-velocity μ-space. In the presence of an external force per unit mass, $\mathbf{F}$, and of a thermal gradient, the function f satisfies the Boltzmann equation.

$$If = \frac{\partial f}{\partial t} + \mathbf{F}\frac{\partial f}{\partial \mathbf{v}} + \mathbf{v}\frac{\partial f}{\partial \mathbf{x}} - \psi(f, f) = 0, \tag{2.1}$$

where the collision operator ψ is independent of t, $\mathbf{x}$, and $\mathbf{F}$. The term "Boltzmann equation" has to be understood here in a wider sense. Indeed, eq. (2.1) includes the usual Boltzmann,[21] as well as the Landau and the ring equations[22] describing dilute plasmas, or the Fokker–Planck equation[23] used in the theory of

Brownian motion. Such equations have a wide domain of applicability in statistical mechanics and kinetic theory. It is possible to extend to generalized kinetic equations for strongly coupled systems the calculations we shall carry out with eq. (2.1), but we shall not develop this here.

Our object is to find a generalized Lagrangian for eq. (2.1), the local potential. This quantity, Φ, will be a continuous differentiable functional of the distribution function: $\Phi = \Phi(f)$. Moreover, it has to yield by some variational procedure (to be defined below) the kinetic eq. (2.1) as an Euler–Lagrange equation, and it should have a minimum corresponding to the solution of this equation. If such a quantity exists, it is intuitively clear that, at least for a certain range of values of the external constraint, the kinetic equation will have solutions exhibiting some stability properties. In other words, suppose that $f_0(t, \{a_i^0\})$ is a solution of eq. (2.1) depending on the values of some parameters $a_i(t)$. Then the solution

$$f(t, \{a_i\}) = f_0(t, \{a_i^0\}) + \Delta_1 f(t, \{a_i^0\}, \{\Delta a_i\}) \tag{2.2}$$

resulting from a change of the parameters $\{a_i\}$ satisfies the relation

$$|\Delta_1 f(t)| < \delta(\eta, t_0) \qquad (\delta > 0, t \geqq t_0 > 0), \tag{2.3a}$$

provided

$$|a_i - a_i^0| < \eta_i \qquad (\eta_i > 0). \tag{2.3b}$$

We shall verify this stability property in great detail in the next sections. At the moment we shall keep in mind and make use of the idea that the local potential should be intimately connected with the deviations $\Delta_1 f$ of the solution f_0 to eq. (2.1), arising from the change of a_i's. It must be realized that these changes occur the much in sense of virtual changes, since the external constraints are on the average kept constant. They ought, therefore, to be attributed rather to random fluctuations, taking place in the system. Such fluctuations may be due, for example, to random instantaneous changes of the external conditions, which immediately afterwards assume their previous values; they can also be thought of as ensemble fluctuations, inherent in the nature of the statistical description of the system. In any case they imply the appearance of random (Langevin)

forces in the system[23] which must be contrasted from the external driving forces $\mathbf{F}$ and $\partial f/\partial \mathbf{x}$.

It is, therefore, very natural to adopt the viewpoint of fluctuation theory and to think of eq. (2.1) as a Langevin equation. It will be convenient to consider that the random force is due to the deviations $\Delta f(t)$ of the distribution function f, not from its unperturbed value f_0 [cf. eq. (2.2)] but rather from a state $\bar{f} = \bar{f}(t, \{a_i^0\}, \{\Delta a^i\})$, depending on the perturbations Δa^i but averaged over their values, a state being therefore a non-fluctuating one. The function $\bar{f}$ will also satisfy eq. (2.1) and will be constructed to be a slowly varying solution. It could be thought of as, for example, a normal solution[21,24] to the kinetic equation. On the other hand, $\Delta f(t)$ will be a rapidly varying function of time. Writing

$$f(t) = \bar{f}(t) + \Delta f(t) \tag{2.4}$$

and replacing in eq. (2.1) we find

$$\frac{\partial \Delta f}{\partial t} + \mathbf{F}\frac{\partial \Delta f}{\partial \mathbf{v}} + \mathbf{v}\frac{\partial \Delta f}{\Delta \mathbf{x}} - \psi(\bar{f}, \Delta f) = \psi(\Delta f, \Delta f), \tag{2.5}$$

where use was made of the fact that $\bar{f}$ satisfies eq. (2.1). The left-hand side of eq. (2.5) is linear in Δf. The non-linear term (right-hand side) can be interpreted as the Langevin force due to the random fluctuations.[25]

For the purpose of constructing the local potential we shall add to eq. (2.5) the equation for $\bar{f}$. This yields

$$\frac{\partial \Delta f}{\partial t} = -\frac{\partial \bar{f}}{\partial t} - F\frac{\partial f}{\partial \mathbf{v}} - \mathbf{v}\frac{\partial f}{\partial \mathbf{x}} + \psi(f, f). \tag{2.6}$$

The time derivative in the left-hand side can be thought of as a perturbed current in μ-space. It is natural to associate to this current a thermodynamic force porportional to Δf. In order to carry the analogy with thermodynamics as far as possible, and also to take advantage of some symmetry properties, we choose this force to be $-\Delta \log f$.*,[20] We multiply both sides of eq. (2.6)

* The symbol Δ, both in Δf and $\Delta \log f$, should be understood here in the sense of fluctuation theory. In particular it should not be confused with the symbol for functional differentiation.

by this quantity and we integrate over μ-space and over time between the initial time of setting up the fluctuating state till a final time T. We obtain:[20]

$$\Psi(f|\bar{f}) = \int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{v} \left(- \frac{\partial \Delta f}{\partial t} \Delta \log f \right)$$

$$= \int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{v} \left[\frac{\partial \bar{f}}{\partial t} \Delta \log f + \left(\mathbf{F} \frac{\partial f}{\partial \mathbf{v}} + \mathbf{v} \frac{\partial f}{\partial \mathbf{x}} \right) \Delta \log f \right.$$

$$\left. - \Delta \log f \psi(f, f) \right]. \quad (2.7)$$

In the left-hand side we limit attention to terms of order $(\Delta f)^2$. Moreover, we neglect the variation of the function $\bar{f}$ over the rapid time scale on which Δf varies. We thus have:

$$\Psi(f|\bar{f}) = -\int \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{v} \frac{1}{2\bar{f}} [(\Delta f(T))^2 - (\Delta f(0))^2]. \quad (2.8)$$

In order to investigate the stability properties of the solutions of eq. (2.1) we shall content ourselves with formulating sufficient criteria. Moreover, we shall be exclusively interested in asymptotic stability properties, i.e. in the case when, instead of eq. (2.3a), we have

$$\lim_{t \to \infty} \Delta_1 f = 0. \quad (2.3a')$$

Taking T sufficiently large in eq. (2.8) and applying eq. (2.3a') we conclude that

$$\Psi(f|\bar{f}) \geqq 0, \quad (2.9a)$$

i.e.

$$\int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{v} \left[\left(\frac{\partial \bar{f}}{\partial \mathbf{v}} + \mathbf{F} \frac{\partial f}{\partial \mathbf{x}} + \mathbf{v} \frac{\partial f}{\partial \mathbf{x}} \right) \Delta \log f \right.$$

$$\left. - \Delta \log f \psi(f, f) \right] \geqq 0. \quad (2.9b)$$

To proceed further, we have to take a specific form for the collision operator, ψ. From now on, we shall restrict our attention to classical statistical mechanics. Moreover, we shall always illustrate our calculations by using the Landau form[22]

$$\psi = \frac{8\pi^4\lambda^2 n}{m}\int d\mathbf{v}'\int d\mathbf{l}|V_l|^2\frac{\partial}{\partial \mathbf{v}}\mathbf{l}\,\delta(\mathbf{lg})$$

$$\times\left(\frac{\partial}{\partial \mathbf{p}}-\frac{\partial}{\partial \mathbf{p}'}\right)\mathbf{l}f_1(\mathbf{x},\mathbf{v},t)f_1(\mathbf{x},\mathbf{v}',t). \quad (2.10)$$

The extension to the Boltzmann and to the ring equation forms of ψ is indicated in Appendix A.

In eq. (2.10), n is the number density, m the mass, V_l the Fourier transform of the interaction between particles, $\mathbf{v}$ the velocity, $\mathbf{p}$ the momentum, $\mathbf{g} = \mathbf{v} - \mathbf{v}'$, and $\delta(\mathbf{lg})$ is a propagator which is actually a delta function. In eq. (2.10) we considered the case of a one-component system. In section 5, we shall see how the results are trivially extended to the many component case. We also recall that eq. (2.10) describes in a realistic way most of the properties of a dilute plasma, provided the intereaction is taken to be a Debye cut-off interaction.

We now replace the form (2.10) into eq. (2.9b); we symmetrize over the two particles and integrate by parts. We get

$$0 \leqq \Psi = \int_0^T dt\int d\mathbf{x}\,d\mathbf{v}\left\{\Delta\left(\frac{\partial \bar{f}}{\partial t}\log f\right)+\left(\mathbf{F}\frac{\partial f}{\partial \mathbf{v}}+\mathbf{v}\frac{\partial f}{\partial \mathbf{x}}\right)\Delta\log f\right\}$$

$$+\frac{2\pi^4\lambda^2 n}{m^2}\int_0^T dt\int d\mathbf{x}\,d\mathbf{v}\,d\mathbf{v}'\int d\mathbf{l}$$

$$\times|V_l|^2 ff'\delta(\mathbf{lg})\Delta\left[\mathbf{l}\left(\frac{\partial}{\partial \mathbf{v}}-\frac{\partial}{\partial \mathbf{v}'}\right)\log ff'\right]^2. \quad (2.11)$$

Clearly in order to construct for eq. (2.1) a generalized Lagrangian having all desired properties we have to integrate eq. (2.11) and determine a functional $\Phi(f|\bar{f})$ such that

$$\Delta\Phi(f|\bar{f}) = \Psi(f|\bar{f}). \quad (2.12)$$

It is easy, however, to convince oneself that for a general form of the distribution function f the quantity (2.11) is not an exact differential (with respect to changes represented by the symbol Δ, see footnote on p. 305). The fundamental idea of the local potential amounts now to extending the meaning of the functionals Φ and Ψ and allowing them to be *functionals of two independent functions*, f and $\bar{f}$. The simplest integrable form that one can then

deduce from eq. (2.11) is the one where the functions f in front of the variational symbol Δ are replaced by their non-fluctuating values, $\bar{f}$. We notice that this does not amount to restricting eq. (2.11) to terms of lower order in Δf, since $\Delta \log f$ already contains arbitrary powers of Δf. One should rather consider it as a prescription, defining a new functional of two functions:

$$\Phi(f,\bar{f}) = \int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{v} \left\{ \left(\frac{\partial f}{\partial t} + \mathbf{F}\frac{\partial \bar{f}}{\partial \mathbf{v}} + \mathbf{v}\frac{\partial \bar{f}}{\partial \mathbf{x}} \right) \log f \right.$$
$$\left. + \frac{2\pi^4\lambda^2 n}{m^2} \int \mathrm{d}\mathbf{v}' \int \mathrm{d}\mathbf{l}\, |V_l|^2 \bar{f}\bar{f}' \delta(\mathbf{l}\mathbf{g}) \left[\mathbf{l} \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'} \right) \log ff' \right]^2 \right\}. \quad (2.13)$$

This is the local potential for eq. (2.1) with the form (2.10) for the collision operator. In order to justify the final step which led us to constructing this functional, we have now to verify the two fundamental properties that it has to fulfil.

(*a*) We first seek under what prescription Φ gives rise to eq. (2.1). Let us require that f be stationary with respect to variations of f, the function $\bar{f}$ being kept fixed. The Euler–Lagrange equations give

$$\frac{\partial \Phi_1}{\partial f} - \frac{\mathrm{d}}{\mathrm{d}\mathbf{v}} \cdot \frac{\delta \Phi_1}{\delta(\partial f/\partial \mathbf{v})} = 0, \quad (2.14a)$$

or, when $\log f$ is considered to be the independent function

$$\frac{\partial \Phi_1}{\partial \log f} - \frac{\mathrm{d}}{\mathrm{d}\mathbf{v}} \cdot \frac{\delta \Phi_1}{\delta(\partial \log f/\partial \mathbf{v})} = 0, \quad (2.14b)$$

where Φ_1 is the integrand in eq. (2.13). Both equations finally yield

$$\frac{\partial \bar{f}}{\partial t} + \mathbf{F}\frac{\partial \bar{f}}{\partial \mathbf{v}} + \mathbf{v}\frac{\partial \bar{f}}{\partial \mathbf{x}} = \frac{8\pi^4\lambda^2 n}{m} \int \mathrm{d}\mathbf{v}' \int \mathrm{d}\mathbf{l}\, |V_l|^2 \frac{\partial}{\partial \mathbf{v}} \mathbf{l}$$
$$\frac{\bar{f}\bar{f}'}{ff'} \delta(\mathbf{l}\mathbf{g}) \mathbf{l} \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'} \right) ff'. \quad (2.15)$$

This equation reduces to the Landau equation provided one puts $f = \bar{f}$. The variational property of Φ has, therefore, to be understood as:

$$\delta\Phi(f,\bar{f})/\delta f = 0, \qquad f = \bar{f} \text{ after variation} \quad (2.16)$$

yields the kinetic equation

$$If = 0. \tag{2.17}$$

This may be also understood as a generalization of the usual variational procedures.[6,14]

It is interesting to note that eq. (2.16) with the condition $f = \bar{f}$ (after variation) amounts to taking the average of eq. (2.15):

$$\overline{\delta\Phi(f,\bar{f})/\delta f = 0.} \tag{2.16a}$$

In addition, one has to assume that

$$\bar{f}\bar{f} = \bar{f}\bar{f},$$

in agreement with our previous restriction to dilute systems.

(*b*) Next we ask whether the external property (2.11) still holds. Since Δf is small we can develop f in eq. (2.13) around $\bar{f}$ and retain terms to order $(\Delta f)^2$ only. Keeping in mind that $\bar{f}$ is a solution to the kinetic equation, we find that

$$\Phi(\bar{f},f) = \Phi(\bar{f},\bar{f}) + \frac{4\pi^4\lambda^2 n}{m^2}\int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{x}\ \mathrm{d}\mathbf{v}\ \mathrm{d}\mathbf{v}'\ \mathrm{d}\mathbf{l}\ |V_l|^2\delta(\mathbf{lg})\bar{f}\bar{f}'$$

$$\left[\mathbf{l}\left(\frac{\partial}{\partial\mathbf{v}} - \frac{\partial}{\partial\mathbf{v}'}\right)\left(\frac{\Delta f}{\bar{f}} + \frac{\Delta f'}{\bar{f}'}\right)\right]^2 \geqq \Phi(\bar{f},\bar{f}), \tag{2.18}$$

where $\Phi(\bar{f},\bar{f})$ is the value of the local potential (2.13) in the non-fluctuating state $\bar{f}$. We see that $\Phi(f,\bar{f})$ takes its minimum value in the non-fluctuating state, provided this state satisfies the kinetic equation. Φ exhibits, therefore, an extremal property in the sense of fluctuation theory. It is essential to notice that in eq. (2.18) the terms linear in Δf have been removed owing to the presence of both convective and collisional terms in the kinetic equation. Furthermore, the difference $\Phi - \Phi(\bar{f},\bar{f})$, depends only on the dissipative processes in the system; in the section 3 we shall comment further on this point.

It is interesting to notice the intimate relation between the local potential and the quantities that one uses in the variational approaches for deriving the linearized kinetic equations.[17,18] In the

case of a linearized kinetic equation one may expand both functions f and $\bar{f}$ around the local equilibrium distribution

$$f^{(0)} = n(\mathbf{x}) \left(\frac{m}{2\pi k T(\mathbf{x})}\right)^{3/2} \exp\left\{-\frac{m[\mathbf{v} - \mathbf{u}(\mathbf{x})]^2}{2kT(\mathbf{x})}\right\}, \tag{2.19}$$

where $T(\mathbf{x})$ is the local temperature and $\mathbf{u}(\mathbf{x})$ the local hydrodynamic velocity. We have

$$\bar{f} = f^{(0)}(1 + \bar{\phi}) \tag{2.20a}$$

and

$$\log f = \log f^{(0)} + \phi + 0(\phi^2). \tag{2.20b}$$

Moreover, the product $f^{(0)}f'^{(0)}$ commutes with the operator $\delta(l\mathbf{g})\mathbf{l}(\partial/\partial\mathbf{v} - \partial/\partial\mathbf{v}')$. We thus obtain (keeping terms to order ϕ^2 only):

$$\Phi(f, \bar{f}) = \int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{v} \left\{\left(\frac{\partial f^{(0)}}{\partial t} + \mathbf{F}\frac{\partial f^{(0)}}{\partial \mathbf{v}} + \mathbf{v}\frac{\partial f^{(0)}}{\partial \mathbf{x}}\right)\phi + \frac{2\pi^4\lambda^2 n}{m^2} \int \mathrm{d}\mathbf{v}' \int \mathrm{d}\mathbf{l} |V_l|^2 \delta(\mathbf{l}\mathbf{g}) f^{(0)} f'^{(0)} \left[\mathbf{l}\left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'}\right)(\phi + \phi')\right]^2\right\}$$
$$\equiv \Phi(\phi). \tag{2.21}$$

This has exactly the form of the potentials usually encountered in the study of self-adjoint forms of the kinetic equation.[17,18] We notice that in this limit the local potential becomes a functional of the function ϕ only. Its rôle as a Lagrangian as well as the variational property $\delta\Phi/\delta\phi = 0$ take therefore their usual significance. We should however keep in mind that in the general case the local potential (2.13) enables us to attack much more general problems, for example nonself-adjoint problems (non-linear theory, system in a magnetic field etc.). In these problems in general one has no more extremal variational principles in the usual sense.[8,9,18] It is remarkable that the use of the local potential allows one to take advantage of the minimum property (2.18). We shall see below how this property may be important in the course of manipulations involving the local potential. We shall also treat an explicit example of a typically nonself-adjoint problem and show how the variational technique used here still works (see also Appendix B).

Finally, it is interesting to evaulate the quantity $\Phi(\bar{f}, \bar{f})$ which, according to eq. (2.18), is the minimum value of the local potential.

From eq. (2.13) one has

$$\Phi(\bar{f},\bar{f}) = \int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{v} \left\{ \frac{\partial \bar{f}}{\partial t} \log \bar{f} + \mathbf{v} \frac{\partial \bar{f}}{\partial x} \log \bar{f} \right.$$

$$\left. - \frac{4\pi^4 \lambda^2 n}{m^2} \log \bar{f} \int \mathrm{d}\mathbf{v}' \int \mathrm{d}\mathbf{l} |V_l|^2 \mathbf{l} \frac{\partial}{\partial \mathbf{v}} \delta(\mathbf{lg})\mathbf{l} \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'} \right) \bar{f}\bar{f}' \right\}. \quad (2.22)$$

The first two terms are minus the time integrals of the time derivative and of the flow of entropy, provided we define the entropy density to be:[21]

$$s = -k \int \mathrm{d}\mathbf{v} f \log f. \quad (2.23)$$

The last term is half the time integral of the entropy production σ. We therefore have

$$\Phi(\bar{f},\bar{f}) = k \int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{x} \left\{ -\frac{\partial s}{\partial t} + \frac{1}{2}\sigma \right\}. \quad (2.24)$$

These interesting properties of the local potential are, of course, due to its particular character as a functional of both functions f and $\bar{f}$. The price we had to pay has been in the lack of symmetry in the way f and $\bar{f}$ appear in eq. (2.13) and, in addition, in the arbitrariness in defining in this expression the functional $\bar{f}$. Indeed, the local potential is not invarient in an infinitesimal change

$$\bar{f}_1 = \bar{f} + \bar{\varepsilon} \quad (2.25)$$

since the equation $\delta\Phi/\delta\bar{f} = 0$ does not imply the kinetic equation. On the other hand, there are several transformations allowed for $\bar{f}$ (after putting $f = \bar{f}$; cf. eq. 2.16) as a solution of the kinetic equation. This lack of symmetry may sometimes serve in redefining $\bar{f}$ in eq. (2.13) and have expressions which have more desirable properties for our specific purposes.[11]

On the other hand we should notice that the two properties (2.14) automatically assure invariance of the local potential in the transformations

$$f_1 = f + \varepsilon \quad (2.26)$$

and

$$\log f_1 = \log f + \delta.$$

Having a quantity, eq. (2.13), exhibiting many properties of a Lagrangian, it is finally interesting to comment on the consequences of its different coordinate symmetries. In particular we may ask how such symmetries are related to the conservation equations, in the same way as the intrinsic symmetry expressed by eq. (2.16) was related to the conservation equation in μ-space, i.e. the kinetic equation. We therefore express the local potential density, defined by

$$\Phi = \int \mathrm{d}t\, \mathrm{d}\mathbf{x}\, \Phi_1(\mathbf{x}, t) \tag{2.27}$$

as invariant under an infinitesimal transformation of coordinates

$$\mathbf{x}'_p = \mathbf{x}_p + \xi_p \qquad (p = 1, 2, 3). \tag{2.28}$$

The change of the local potential density is given by

$$\delta\Phi_1 = \xi_p \frac{\partial \Phi_1}{\partial \mathbf{x}_p}. \tag{2.29a}$$

The translational invariance requires that Φ_1 does not depend explicitly on $\mathbf{x}$; therefore,

$$\begin{aligned}\partial\Phi_1 &= \frac{\delta\Phi_1}{\delta\bar{f}}\,\delta\bar{f} + \frac{\delta\Phi_1}{\delta \log f}\,\delta \log f + \frac{\partial\Phi_1}{\delta(\partial \log f/\partial v)}\,\delta\left(\frac{\partial \log f}{\partial v}\right) \\ &= \xi_\nu \left\{\frac{\delta\Phi_1}{\delta\bar{f}}\frac{\partial\bar{f}}{\partial \mathbf{x}_\nu} + \frac{\delta\Phi_1}{\delta \log f}\frac{\partial \log f}{\partial \mathbf{x}_\nu} + \frac{\delta\Phi_1}{\delta(\partial \log f/\partial v)}\frac{\partial}{\partial \mathbf{x}_\nu}\frac{\partial \log f}{\partial \mathbf{v}}\right\}\end{aligned} \tag{2.29b}$$

On the other hand, the local potential gives rise to the eq. (2.14b). Here we do not yet use the kinetic eq. (2.17), i.e. we do not yet put $f = \bar{f}$. We simply consider eq. (2.14b) to be the Euler–Lagrange equation for the given local potential. Using this equation and equating the two expressions (2.29a) and (2.29b) for $\delta\Phi_1$ we find

$$\frac{\partial\Phi_1}{\partial \mathbf{x}_\mu} - \frac{\delta\Phi_1}{\delta\bar{f}} \cdot \frac{\partial\bar{f}}{\partial \mathbf{x}_\mu} = 0, \tag{2.30}$$

where we also assumed that the functions f and $\bar{f}$ tend sufficiently rapidly to zero as $|\mathbf{v}| \to \infty$. Developing eq. (2.27) a little further by expressing $\delta\Phi_1/\delta\bar{f}$ from eq. (2.13) and using again eq. (2.14b), we find

$$\int \mathrm{d}\mathbf{v}\,\mathrm{d}\mathbf{v}'\,\frac{\partial \log \bar{f}}{\partial \mathbf{x}}\left\{\frac{\partial f}{\partial t}+\mathbf{v}\nabla \bar{f}-\frac{8\pi^4\lambda^2 n}{m^2}\int \mathrm{d}\mathbf{l}\,|V_l|^2\mathbf{l}\,\frac{\partial}{\partial \mathbf{v}}\right.$$

$$\left.\times\,\delta(\mathbf{l}\dot{\mathbf{g}})\mathbf{l}\left(\frac{\partial}{\partial \mathbf{v}}-\frac{\partial}{\partial \mathbf{v}'}\right)\log \bar{f}\bar{f}'\right\}=0. \quad (2.31)$$

If we now put $f=\bar{f}$ we see that eq. (2.28) reduces to the three hydrodynamic equations of conservation[3,21] provided, f is further developed around local equilibrium. For more general form of f, eq. (2.31) may generate further moment equations associated with the kinetic equation.

We therefore see how the local potential is connected with the conservation properties of the system, in the same way as Lagrangians are in field theories. Such invariance properties of the local potential should be taken into account seriously in any practical use; for example, the choice of trial functions used in an approximated solution generated by the local potential should be restricted in such a way that the different conservation laws are always satisfied.

3. CONVERGENCE PROPERTIES AND FLUCTUATION THEORY

We have already established the minimum property of the local potential, expressed by eq. (2.18). We have also seen that in the minimum state the function $\bar{f}$ is a solution of the kinetic equation averaged over all fluctuations. Therefore, it should be related with the macroscopic properties and phenomenological laws in the system, for example, Fourier's law of heat conduction, Gibbs's expression for entropy production, etc. Now in many physical situations we can expect that the average state $\bar{f}$ and the macroscopic states associated with it correspond also to the most probable states that the system can reach. In other words, among all individually fluctuating states that the system (which always satisfies the kinetic equation) can reach, the most probable state corresponds to a non-fluctuating situation. This clearly suggests that the local potential should be related to the probability of a fluctuation around the state $\bar{f}$. We shall verify this in the domain of validity of the Einstein fluctuation formula.[3]

This is expected to be true, at least when attention is restricted to small deviations from the average state $\bar{f}$, in which case one can expect that local formulation of statistical mechanics of non-uniform systems should still be possible.[3,5] Let us therefore assume that the probability of a fluctuation in the functional space of f's is

$$p[\Delta f] = c \exp \frac{1}{k} \int \mathrm{d}\mathbf{x}\, \Delta s \tag{3.1}$$

where c is some normalization constant.

We shall prove that under this assumption the state $\bar{f}$ corresponds to the most probable one and that, consequently, eq. (2.15) gives the most probable state to be realized when the state $\bar{f}$ is unchanged.

In eq. (2.23) we have already defined the entropy density. In the state $\bar{f}$ the same definition should, of course, apply:

$$\bar{s} = -k \int \mathrm{d}\mathbf{v}\, \bar{f} \log \bar{f}. \tag{3.2a}$$

It is, however, more convenient to define the entropy excess Δs, measured from the state $\bar{f}$, not simply as

$$-k \int \mathrm{d}\mathbf{v}\, (f \log f - \bar{f} \log \bar{f})$$

but rather by means of an expression similar to that used in the theory of fluctuations around an equilibrium state.[23,26] More precisely, we shall weight the function under the logarithm by the measure of the non-fluctuating state:

$$\Delta s = -k \int \mathrm{d}\mathbf{v}\, f \log f/\bar{f}. \tag{3.2b}$$

This expression satisfies all necessary conditions, for example, $\Delta s[f = \bar{f}] = 0$, and in the case of fluctuations around equilibrium ($\bar{f} = f^{\mathrm{eq}}$) it reduces to the well-known theory.[26] We should also notice that the validity of definitions (3.2) is restricted to dilute systems.[21,22] We can further write eq. (3.1) as

$$p[\Delta f] = c \exp \frac{1}{k} \int \mathrm{d}\mathbf{x} \int_0^T \mathrm{d}t\, \frac{\partial \Delta s}{\partial t};$$

or, putting $f = \bar{f} + \Delta f$,

$$\begin{aligned} p[\Delta f] &= c \exp \int \mathrm{d}\mathbf{x} \int_0^T \mathrm{d}t \left[- \log f \frac{\partial f}{\partial t} + \log \bar{f} \frac{\partial f}{\partial t} + \frac{f}{\bar{f}} \frac{\partial \bar{f}}{\partial t} \right] \\ &= c \exp \int \mathrm{d}\mathbf{x} \int_0^T \mathrm{d}t \left[- \frac{\partial \Delta f}{\partial t} \Delta \log f + \left(\Delta \log f - \frac{\Delta f}{\bar{f}} \right) \frac{\partial \bar{f}}{\partial t} \right]. \end{aligned} \tag{3.3}$$

Since $\bar{f}$ is a slowly varying function of time, we may neglect the last term in the brackets. The first term is just the variation of the local potential changed in sign (cf. eq. 2.7). We may therefore write

$$\begin{aligned} p[\Delta f] &= c \exp \left[\Phi(\bar{f}, \bar{f}) - \Phi(f, \bar{f}) \right] \\ &= c \exp \left(- \Delta \Phi \right). \end{aligned} \tag{3.4}$$

This equation precisely establishes the connection we were looking for between $p[\Delta f]$ and Φ. Another interesting consequence of eqs. (3.1) and (3.2) can be seen when one develops f around $\bar{f}$ and retains terms to order $(\Delta f)^2$ at most. The terms of Δs linear in Δf simplify and one obtains

$$p[\Delta f] = c(\bar{f}) \exp \left[- \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{v} \frac{(\Delta f)^2}{2\bar{f}} \right]. \tag{3.5}$$

This formula shows that in the present approximation there is no correlation of the fluctuation of f in different regions of μ-space. Moreover it gives, for specific values $(\mathbf{x}_0, \mathbf{v}_0)$ of $(\mathbf{x}, \mathbf{v})$, a relation between the mean square deviation of the fluctuations of f and the average distribution $\bar{f}$:

$$\overline{(\Delta f)^2}_{x_0, v_0} = \bar{f} \delta(\mathbf{x} - \mathbf{x}_0) \delta(\boldsymbol{u} - \boldsymbol{u}_0), \tag{3.6}$$

the average being taken over $p[\Delta f]$.

The extreme simplicity of this result is due to the fact that we have been interested in correlating fluctuations at the same point in μ-space. When fluctuations at different points are involved the formulae become much more complicated and contain the correlations between particles in an explicit way.[25] As it stands, however, formula (3.6) is in complete agreement with the theory of fluctuations of the distribution functions developed by Klimontovitch[27] and Kadomtsev.[25] Indeed, in this theory the correlation of fluctuations is given by a term like that in the

right-hand side of eq. (3.6) plus a term proportional to the non-fluctuating two-body correlation function, $\bar{g}(\mathbf{v}, \mathbf{v}')$. It is this term that gives rise to correlation of fluctuations in different points in μ-space which, as we have already mentioned, cannot appear in the approximation we are considering here. Indeed, we have used definitions (3.2) which are satisfactory only in the case of the lowest approximation corresponding to a dilute system.[21,22] Now, in such a case the influence of the correlation function is negligible in the different transport processes, and the second term in the approaches of Klimontovitch and Kadomtsev also becomes negligible. Thus we get an agreement between the two approaches in the case under consideration. To extend the agreement to the more general case of non-negligible correlations, one clearly has to generalize the entropy definition (3.2) to include correlations explicitly. This amounts to defining entropy in a strongly coupled, non-equilibrium system; this is an unsolved problem, although some progress has been realized recently in this direction.[28] Approximate expressions can be given for some special cases such as those near local equilibrium, where the Gibbs formula still holds.[3,26] We shall not, however, develop this point further.

It is remarkable to notice that the fundamental properties of the local potential that we have presented so far are all related to its minimum property, which makes it closely related to a Lagrangian. From eq. (2.13) we see that the part Φ_{col} of the local potential due to the contribution of the purely dissipative processes (collisions) is positive definite. On the other hand, the convection part Φ_{conv}, associated with the first three terms in the right-hand side of eq. (2.13), does not have a definite sign and contains terms linear in the fluctuation Δf. It was demonstrated above, however, that the combination of these two terms gives a quantity having a minimum property and in which the terms that are linear in Δf are removed (cf. eq. 2.18). This property clearly suggests that what gives the local potential its physical significance is the presence of dissipation and that in the presence of purely convective processes it loses its meaning. Indeed, it has no longer a minimum property and, in addition, vanishes when $\bar{f}$ becomes the correct solution of the kinetic equation (without dissipation). The physical significance of the local potential,

particularly its connection with fluctuation theory, is therefore lost.

At this point it is pertinent to make the connection with the technical aspect of the local potential as a means for calculating the distribution $\bar{f}$ or for deducing a stability criterion for the system. This is actually one of the purposes that variational principles have always served. Let us follow a Rayleigh–Ritz scheme[6,14] and develop both unknown functions f and $\bar{f}$ in a complete set of orthogonal functions u_i:

$$f = \sum_i c_i(t) u_i(\mathbf{x}, \mathbf{v}) \tag{3.7a}$$

and

$$\bar{f} = \sum_i \bar{c}_i(t) u_i(\mathbf{x}, \mathbf{v}), \tag{3.7b}$$

assuming from now on that all physically admissible solutions of the kinetic equation should admit such expansions. The problem is now reduced to the calculation of the coefficients c_i. The local potential becomes a function of c_i and $\bar{c}_i$, and the stationary property of Φ (see eq. 2.16) is expressed by the system of algebraic equations:

$$\frac{\partial \Phi(\{c_i\}, \{\bar{c}_i\})}{\partial c_m} = 0 \quad (m = 1, 2, \ldots, n \ldots) \tag{3.8}$$

$$c_i = \bar{c}_i \quad \text{(after variation)}.$$

Using the explicit forms (2.13) and (2.10) we may write these equations as

$$\sum_j \int d\mathbf{x}\, d\mathbf{v}\, u_m \int_0^T dt \left\{ \frac{u_j}{\sum \bar{c}_i u_i} \frac{\partial c_j}{\partial t} + \mathscr{D}_j \bar{c}_j - \mathscr{C}_j \bar{c}_j \right\} = 0 \tag{3.9}$$

$$(m = 1, 2, \ldots, n, \ldots)$$

where

$$\mathscr{D}_i = \frac{1}{\sum_i \bar{c}_i u_i} \left[\mathbf{F} \frac{\partial u_i}{\partial \mathbf{v}} + \mathbf{v} \frac{\partial u_i}{\partial \mathbf{x}} \right] \tag{3.10}$$

and

$$u_j = \frac{1}{\sum_i \bar{c}_i u_i} \psi(\bar{f}, u_j). \tag{3.11}$$

Approximate solutions may now be sought by truncating equations (3.9) to a finite, relatively small number n. Correspondingly,

the local potential becomes a function, Φ_n of $2n$ parameters c_i and $\bar{c}_i$, and eq. (3.8) provides an approximation to the solution of the kinetic equation. Alternatively, when condition $c_i = \bar{c}_i$ is not yet required, the same equation provides an approximation scheme for solving the kinetic equation by iteration, first starting by a known $\bar{c}_i$, then determining the c_i's, which are next used as starting functions for the second iteration, etc. In order to be specific we shall call the two forms of the system of eqs. (3.8), with or without the condition $c_i = \bar{c}_i$, the self-consistent system and the iterative system of equations, respectively.

Let us now go back to the n'th approximate of the system (3.9). Clearly the equations express the fact that the left-hand side of the kinetic eq. (2.17) is orthogonal to the n functions

$$u_m / \sum \bar{c}_i u_i \quad (m = 1, 2, \ldots, n)$$

These functions are linearly independent in the same way as u_m are. We can say, therefore, that eqs. (3.9) result from a particular way of solving the kinetic equation by expressing the orthogonality properties with respect to a particular set of functions.

This method for solving differential or integro-differential equations is known as Galerkin's method.[6,14] Actually, in a normal application of this method (we notice that the Galerkin method need not necessarily be combined with a variational principle) to eq. (2.17) one would have expressed the orthogonality conditions in the form

$$\int \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{v} u_m I(c\bar{c}_i) = 0 \tag{3.12}$$

without using the system of functions $u_m / \Sigma \bar{c}_i u_i$ which introduce a highly non-linear dependence in $\bar{c}_i$. In any case, we clearly see how the self-consistent method for solving the kinetic equation is related to the Galerkin method. The correspondence would be even closer if, instead of the local potential (2.13), we had written a pseudo-Lagrangian using f instead of $\log f$. Equations (3.9) would then be identical with the Galerkin eqs. (3.12). Such a "Lagrangian", however, would simply be a means of calculation, without having the minimum property mentioned above or any connexion with the fluctuation properties of the system. In addition it would become identically zero for the solution $\bar{f}$ to the kinetic equation.

It is reasonable to expect that advantage will accrue from using our functional (2.13) that combines the necessary physical requirement to be a Lagrangian in a generalized sense with the property of yielding variational equations similar to Galerkin's. Particularly in approximate calculations it could happen that the variational approach gives safer results than would be obtained by truncating expansions (3.7) to a small n and then applying Galerkin's method. Indeed, one sometimes finds results quite sensitive to the choice of trial functions $\{u_j\}$.[7]

Another interesting property of the local potential is that it may assure the convergence of an approximate procedure to solve the kinetic equation, based on eqs. (3.8). Such a property of the local potential is far from trivial. Indeed, eqs. (3.8) or (3.9) are non-self-adjoint and, in general, non-linear. Under those circumstances it turns out to be very hard to prove the convergence of the Galerkin method[6,14] or even to construct a variational principle in the usual sense. It is, therefore, a most welcome property of the local potential that its minimal character allows the convergence of the variational procedures to be proved. It has been shown rigorously by Glansdorff,[10] quite recently, for the case of the macroscopic thermal conduction problem, and the same method was later applied to the kinetic equation by the author and Ph. Sels.[30] The proof proceeds in two main steps, corresponding to the dual character of the local potential viewed as the generator of the two systems of eq. (3.8), with $c_i \neq \bar{c}_i$ and with $c_i = \bar{c}_i$ (self-consistent system). In the first of the two systems it is understood that (3.7b) corresponds to the exact solution of the problem.

In order to exhibit the main steps of the proof in a clear way, we shall apply it only to a simple version of the Landau equation. It will turn out that the convergence is established without any further assumption about the solutions of this equation. In Appendix C we give a proof for the convergence of the iterative solution of the equation.

We consider the kinetic equation

$$F \frac{\partial f}{\partial v} = \zeta \frac{kT}{m} \cdot \frac{\partial}{\partial v} \left(\frac{mv}{kT} + \frac{\partial}{\partial v} \right) f, \tag{3.13}$$

known as the Fokker–Planck equation.[23,26] It describes the

diffusion of a heavy particle of mass m in a uniform fluid at temperature T characterized by the friction constant ζ, under the action of the driving force F. This equation can be deduced from the Landau equation by considering stationary and uniform systems. Moreover, one has to develop the collision operator in inverse powers of the mass and retain the only non-vanishing terms as the limit of infinitely heavy particles is taken. Normally this equation is written in a three-dimensional system; however, we shall first discuss the one-dimensional case in order to avoid cumbersome notations.

It is convenient to write eq. (3.13) in the form

$$F \frac{\partial f}{\partial v} = \zeta \frac{kT}{m} \cdot \frac{\partial}{\partial v} f_e \frac{\partial}{\partial v} \cdot \frac{f}{f_e}, \tag{3.14}$$

f_e being the equilibrium distribution function. Because of the linear (but non-self-adjoint!) character of the equation, it will be sufficient to construct the local potential by using the quantity f/f_e rather than the $\log f$ used in Section 2.

The result is

$$\Phi = \int \mathrm{d}v \left\{ F \frac{\partial \bar{f}}{\partial v} \frac{f}{f_e} + \frac{\zeta kT}{2m} f_e \left(\frac{\partial}{\partial v} \frac{f}{f_e} \right)^2 \right\}, \tag{3.15}$$

where we use a local potential density per unit time and volume. Indeed, the time and space integrations can be performed explicitly since the system is assumed to be stationary and homogeneous.

By parametrizing in the same way as in eq. (3.7) we get for the nth approximation the two systems of equations:

$$\int \mathrm{d}v \frac{u_m}{f_e} \left[F \frac{\partial \bar{f}}{\partial v} - \frac{\zeta kT}{m} \frac{\partial}{\partial v} f_e \frac{\partial}{\partial v} \frac{f_n}{f_e} \right] \qquad (m = 1, 2, \ldots, n) \tag{3.16}$$

$$\int \mathrm{d}v \frac{u_m}{f_e} \left[F \frac{\partial f_n^*}{\partial v} - \frac{\zeta kT}{m} \frac{\partial}{\partial v} f_e \frac{\partial}{\partial v} \frac{f_n^*}{f_e} \right] \qquad (m = 1, 2, \ldots, n) \tag{3.17}$$

with

$$f_n = \sum_{i=1}^{n} c_i u_i \tag{3.18a}$$

and

$$f_n^* = \sum_{i=1}^{n} c_i^* u_i. \tag{3.18b}$$

It is understood that f_n^* represents the n'th approximation to the self-consistent problem, which is actually the approximate solution of the kinetic equation itself, whereas f_n is the solution of a problem where $\bar{f}$ was already given its correct value as a solution of the kinetic equation.

The important fact is that eq. (3.16) correspond to a usual Rayleigh–Ritz problem.[6,14] The convergence of the unknown function f to the real solution will therefore be proved, provided that one demonstrates that the different approximations to the local potential form a minimal sequence:

$$\Phi_n \geqq \Phi_{n+1} \geqq \ldots \tag{3.19a}$$

Indeed, since we know the local potential exhibits a minimum at $f = \bar{f}$, the sequence of Φ_n's will then necessarily reach this minimum as $n \to \infty$, and consequently f_n will reach the value $\bar{f}$.

We have (see also eq. 3.18a):

$$\Phi_n = \int dv \left\{ F \frac{\partial \bar{f}}{\partial v} \left(\frac{f_{n+1}}{f_e} - \frac{c_{n+1} u_{n+1}}{f_e} \right) + \frac{\zeta k T}{2m} f_e \left[\frac{\partial}{\partial v} \left(\frac{f_{n+1}}{f_e} - \frac{c_{n+1} u_{n+1}}{f_e} \right) \right]^2 \right\} \tag{3.20}$$

or else

$$\Phi_n = \Phi_{n+1} + \int dv \left[F \frac{\partial \bar{f}}{\partial v} \frac{c_{n+1} u_{n+1}}{f_e} - \frac{\zeta k T}{m} f_e \frac{\partial}{\partial v} \frac{f_{n+1}}{f_e} \frac{\partial}{\partial v} \frac{c_{n+1} u_{n+1}}{f_e} + \frac{\zeta k T}{2m} f_e \left(\frac{\partial}{\partial v} \frac{c_{n+1} u_{n+1}}{f_e} \right)^2 \right]. \tag{3.21}$$

The first two terms in the bracket cancel when eq. (3.16) is taken into account. We therefore have:

$$\Phi_n = \Phi_{n+1} + \frac{\zeta k T}{2m} f_e \left(\frac{\partial}{\partial v} \frac{c_{n+1} u_{n+1}}{f_e} \right)^2 \geqq \Phi_{n+1} \tag{3.22}$$

which establishes eq. (3.19). The solution f_n tends therefore to $\bar{f}$. In other words, putting

$$\varepsilon_n = f_n - \bar{f}. \tag{3.23a}$$

we have

$$\lim_{n \to \infty} \varepsilon_n = 0. \tag{3.23b}$$

It is even possible to estimate in this case the error in the n'th approximate to the solution.[6]

Let us call

$$\theta_n = f_n^* - f_n. \tag{3.24}$$

It is clear that the convergence of the self-consistent method will be proved provided we can demonstrate that

$$\lim_{n\to\infty} |\theta_n| \leqq \lim_{n\to\infty} |\varepsilon_n| = 0. \tag{3.25}$$

At the same time we shall have an estimate of the error in the n'th approximation. We see how critically the two steps in the convergence proof use the minimum property of Φ.

To demonstrate eq. (3.25) we subtract eqs. (3.16) and (3.17), multiply the difference by $(c_m^* - c_m)$, and sum over m running from 1 to n. We obtain:

$$\int \mathrm{d}v \, \frac{\theta_n}{f_e}\left[F\,\frac{\partial(\varepsilon_n + \theta_n)}{\partial v} - \frac{\zeta kT}{m}\,\frac{\partial}{\partial v}\left(\frac{\partial}{\partial v}\,\frac{\theta_n}{f_e}\right) f_e\right] = 0; \tag{3.26}$$

or, integrating by parts with respect to v,

$$\frac{\zeta kT}{m}\int \mathrm{d}v \left(\frac{\partial}{\partial v}\,\frac{\theta_n}{f_e}\right)^2 f_e = F\int \mathrm{d}v \,\frac{\partial \theta_n/f_e}{\partial v}\,(\varepsilon_n + \theta_n). \tag{3.27}$$

Applying the Schwartz inequality[6,14] in the right-hand side and dividing through by

$$\left[\int \mathrm{d}v \left(\frac{\partial \theta_n/f_e}{\partial v}\right)^2 f_e\right]^{1/2}$$

we have

$$\frac{\zeta kT}{mF}\left[\int_{-\infty}^{\infty} \mathrm{d}v \left(\frac{\partial \theta_n/f_e}{\partial v}\right)^2 f_e\right]^{1/2} \leqq \left(\int_{-\infty}^{\infty} \mathrm{d}v \frac{|\varepsilon_n|^2}{f_e}\right)^{1/2} + \left(\int_{-\infty}^{\infty} \mathrm{d}v \,\frac{|\theta_n|^2}{f_e}\right)^{1/2} \tag{3.28}$$

To proceed further we have to estimate the integral of the derivative of θ_n/f_e in the left-hand side. To this end we expand θ_n/f_e in series of orthogonal functions with f_e as weight function, e.g. in series of Hermite polynomials*

* The sum in (3.29) starts with $n = 1$ since

$$b_0 = \int_{-\infty}^{\infty} \mathrm{d}v (\theta_n/f_e) H_0 = \int_{-\infty}^{\infty} \mathrm{d}v (\theta_n/f_e) = 0$$

by virtue of the normalization conditions.

$$\theta_n/f_e = \sum_{n=1}^{\infty} b_n H_n \left(\left(\frac{m}{2kT}\right)^{1/2} v\right). \tag{3.29}$$

We then have

$$\int_{-\infty}^{\infty} \mathrm{d}v(\theta_n/f_e)^2 f_e = \left(\frac{2kT}{m}\right)^{1/2} \sum_{ns} b_n b_s \int_{-\infty}^{\infty} \mathrm{d}\xi\, f_e(\xi) H_n H_s$$

$$= \left(\frac{2kT}{m}\right)^{1/2} \sum_{n=1}^{\infty} b_n^2 N_n. \tag{3.30}$$

Where we used reduced variables,

$$\xi = v\left(\frac{m}{2kT}\right)^{1/2} \tag{3.31}$$

and the norm N_n is

$$N_n = \int_{-\infty}^{\infty} \mathrm{d}\xi\, \mathrm{e}^{-\xi^2} H_n^2(\xi) = \sqrt{\pi}\,.\, n\,! 2^n \tag{3.32}$$

On the other hand (see eq. 3.29 and ref. 29),

$$\frac{\partial \theta_n/f_e}{\partial v} = \sum_{n=1}^{\infty} b_n \frac{dH_n}{\mathrm{d}v} = \left(\frac{m}{2kT}\right)^{1/2} \sum_{n=1}^{\infty} 2n b_n H_{n-1} \tag{3.33}$$

and

$$\left(\frac{2kT}{m}\right)^{1/2} \int_{-\infty}^{\infty} \mathrm{d}v\, f_e \left(\frac{\partial \theta_n/f_e}{\partial v}\right)^2 = \sum_{n=1}^{\infty} 4n^2 b_n^2 N_{n-1} = \sum_{n=1}^{\infty} 2n b_n^2 N_n. \tag{3.34}$$

Since

$$\sum_{n=1}^{\infty} 2n b_n^2 N_n \geqq 2 \sum_{n=1}^{\infty} b_n^2 N_n, \tag{3.35}$$

we have

$$\int_{-\infty}^{\infty} \mathrm{d}v \left(\frac{\partial \theta_n/f_e}{\partial v}\right)^2 f_e \geqq \left(\frac{m}{kT}\right) \int_{-\infty}^{\infty} \mathrm{d}v\, \frac{\theta_n^2}{f_e};$$

and eq. (3.28) becomes

$$\left(\left(\frac{kT}{m}\right)^{1/2} \frac{\zeta}{F} - 1\right)\left(\int_{-\infty}^{\infty} \mathrm{d}v\, \frac{|\theta_n|^2}{f_e}\right)^{1/2} \leqq \left(\int_{-\infty}^{\infty} \mathrm{d}v\, \frac{|\varepsilon_n|^2}{f_e}\right)^{1/2}. \tag{3.36}$$

This establishes the convergence condition (3.25) provided that

$$F < \left(\frac{kT}{m}\right)^{1/2} \zeta. \tag{3.37}$$

The self-consistent method for solving eq. (3.13) converges, therefore, towards the solution of that equation provided the dissipative processes (measured by the magnitude of ζ) inside the system dominate the purely convective processes (measured by the magnitude of F). It will be interesting to notice the formal ressemblance between a condition of the type (3.37) and the stability condition for the solutions of the kinetic equation, that we shall discuss in Section 5. On the other hand, condition (3.37) does not seem to be directly related to the conditions of existence of Chapman–Enskog solutions to the kinetic equation,[21] at least for the present example of the Fokker–Planck eq. (3.13). Indeed, such conditions would require the convergence of series expansions in powers of a parameter proportional to the ratio of the two sides of inequality (3.37). This would mean that the stronger inequality

$$F \ll \left(\frac{kT}{m}\right)^{1/2} \zeta \tag{3.38}$$

had to be fulfilled.

It is also necessary to notice that the rapidity of convergence of the procedure depends on the value of the difference $[F - (kT/m)^{1/2}\zeta]$. If, for example, this difference is very small the convergence of the self-consistent method will be very slow, since even for n large one could still have appreciated deviations θ_n.

4. STABILITY THEORY

4.1. The Role of the Local Potential

In this Section we shall apply the method of local potential to some physical problems. Two classes of possible application are immediately suggested by the similarity between the local potential and a usual Lagrangian. First, to determine quasi-steady solutions of the kinetic equation, and, secondly, to study the stability properties of these equations. Both kinds of problem have been investigated in some detail for the macroscopic equations of evolution.[4,12,13] A study of some steady-state problems

from the kinetic equation point of view has been given by Strieder.[31] As for the stability properties, a certain number of points have been studied[20,30] and will now be developed in some detail.

It is well known that stability properties of systems at equilibrium are conveniently studied in terms of functionals such as the thermodynamic potentials (free energy, etc.).[2] A functional playing a comparable rôle near equilibrium is entropy production.[3,17,18] At the same time, stability properties of general dynamical systems far from equilibrium can sometimes be handled successfully by the Lyapounoff methods.[1] Among these, Lyapounoff's second method has proved very convenient in describing some aspects of the stability problem in a very compact form; it is restricted mainly to the study of ordinary first-order systems of differential equations, linear or non-linear, in the form:

$$\frac{\mathrm{d}f_i}{\mathrm{d}t} = Q_i(t, f_1, \ldots, f_n) \qquad (i = 1, 2, \ldots, n) \tag{4.1}$$

It has been proved[1,16] that, if there exist a functional

$$V = V(f_i t) \tag{4.2}$$

which is positive (or negative) semidefinite in some set of values of the real variables (f_i, t) and whose derivative along a solution of the system (4.1)

$$V' = \frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\partial V}{\partial t} + \sum_{i=1}^{n} \frac{\delta V}{\delta f_i} \frac{\mathrm{d}f_i}{\mathrm{d}t} \tag{4.3}$$

is negative (positive) definite, then the unperturbed solution of system (4.1) is stable in the sense of Section 1.

For partial differential equations of the first order in time, some of the Lyapounoff theorems have been generalized by Fowler and Zubov.[32] In particular, Fowler has studied the stability properties of the Vlassov equation; he constructed a Lyapounoff functional combining the two properties mentioned above, and related it to the theremodynamic properties of the system (free energy, etc.).

On the other hand, we have seen in Section 2 that the local potential is a definite function whose variation (this time in the sense of fluctuation theory) is positive definite when the system

is stable. It is therefore pertinent to ask whether there is a relationship between a Lyapounoff functional and the local potential.* This is quite a difficult question to answer in general, since the local potential is associated with partial first-order integro-differential equations, so we shall simply verify in a very simple example that the local potential is a Lyapounoff functional and leave the general case untreated.

We consider the simplified time-dependent kinetic equation[26]

$$\frac{\partial f}{\partial t} + \mathbf{F}\frac{\partial f}{\partial \mathbf{v}} = -\nu(f - f_e) \tag{4.4}$$

describing the relaxation of a uniform system to the equilibrium state f_e with a single relaxation frequency ν (real constant). Following the lines of Sections 2 and 3 we can immediately write a local potential per unit time and volume

$$\Phi(f, \bar{f}) = \int \mathrm{d}\mathbf{v}\left[\left(\frac{\partial \bar{f}}{\partial t} + \mathbf{F}\frac{\partial \bar{f}}{\partial \mathbf{v}}\right)\left(f - f_e\right) + \frac{\nu}{2}\left(f - f_e\right)^2\right] \tag{4.5}$$

This quantity should be understood to be a generator of two differential equations $\delta\Phi/\delta f = 0$ with or without $f = \bar{f}$: Equation (4.4) and

$$\frac{\partial \bar{f}}{\partial t} + \mathbf{F}\frac{\partial \bar{f}}{\partial \mathbf{v}} = -\nu(f - f_e). \tag{4.6}$$

When $\bar{f}$ is a solution of eq. (4.6) the local potential becomes

$$\Phi(f) = -\frac{\nu}{2}\int \mathrm{d}\mathbf{v}\,(f - f_e)^2 < 0, \tag{4.7}$$

provided $\nu > 0$, a condition which is of course always satisfied.

Let us now calculate the time derivative of Φ:

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t} = \int \mathrm{d}\mathbf{v}\left[\left(\frac{\partial \bar{f}}{\partial t} + \mathbf{F}\frac{\partial \bar{f}}{\partial \mathbf{v}}\right)\frac{\partial \bar{f}}{\partial t} + (f - f_e)\left(\frac{\partial^2 \bar{f}}{\partial t^2} + \mathbf{F}\frac{\partial^2 f}{\partial t \partial \mathbf{v}}\right) + \nu(f - f_e)\frac{\partial f}{\partial t}\right] \tag{4.8}$$

* It should be emphasized that a Lyapounoff functional character of the local potential is not to be confused with its extremal character, Eq. (2.18).

Using eqs. (4.4) and (4.6) we find

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t} = -\nu \int \mathrm{d}\mathbf{v}\,(f - f_e)\left[-\mathbf{F}\frac{\partial f}{\partial \mathbf{v}} - \nu(f - f_e)\right]. \tag{4.9}$$

We see that $\mathrm{d}\Phi/\mathrm{d}t > 0$ provided that

$$\int \mathrm{d}\mathbf{v}\,(f - f_e)\left[\mathbf{F}\frac{\partial f}{\partial \mathbf{v}} + \nu(f - f_e)\right] > 0;$$

or, using eq. (4.4),

$$\int \mathrm{d}v\,\frac{\partial (f - f_e)^2}{\partial t} < 0. \tag{4.10}$$

This is precisely a stability condition for the system. Indeed, when eq. (4.10) is satisfied, the function f approaches f_e as t approaches infinity. Alternatively, eq. (4.10) expresses that the entropy production of the system is positive in a stable state.*

We see that the local potential, if it exists, may be a Lyapounoff functional of the two functions $f, \bar{f}$ satisfying differential equations of the forms (4.4) and (4.6). The inverse is not always true, i.e. a Lyapounoff functional for a kinetic equation is not necessarily identical with the local potential. Indeed, it is *a priori* possible to construct Lyapounoff functionals even in non-dissipative systems, as in systems described by the Vlassov equation.[32] In such cases the local potential has no physical meaning, as it was shown in detail in Section 3. Yet it is our opinion that further elucidation of the connexion between the local potential and the Lyapounoff functional approach to stability could prove very useful for analyzing many interesting properties of systems for which a local potential can be written, such as the determination of different classes of constant of motion, etc.

* It is well known that in the case of linearized kinetic equations the function $H = \int \mathrm{d}\mathbf{v}(f - f_e)^2$ satisfies an H-theorem.[21] Notice that this function also can be considered to be a Lyapounoff functional, since $H > 0$ and $\mathrm{d}H/\mathrm{d}t < 0$ along the solution of the kinetic eq. (4.4). On the other hand, the function, $H = \int \mathrm{d}\mathbf{v}\, f \log f$ is not a Lyapounoff functional, since both $H < 0$ and $\mathrm{d}H/\mathrm{d}t < 0$.

4.2. Linear Stability Analysis

We shall now investigate the stability properties of quasi-steady-state solutions of the kinetic equation describing a non-uniform system in an external field. We assume there exists such a solution, $f_0(\mathbf{x}, \mathbf{v}, t)$ and study the time behaviour of a random fluctuation $\varepsilon(\mathbf{x}, \mathbf{v}, t)$ (in the sense of Section 2) from this state. The appearance of such a perturbation leads the system to a fluctuating state

$$f(t) = f_0 + \varepsilon(t). \tag{4.11}$$

In the same way the non-fluctuating solution $\bar{f}$ of the same kinetic equation will in general deviate from f_0 by some amount $\bar{\varepsilon}(t)$ which may be thought of as an average of $\varepsilon(t)$ over all perturbations:

$$\bar{f}(t) = f_0 + \bar{\varepsilon}(t). \tag{4.12}$$

In this study we shall investigate only the linear stability of the system. We shall thus be able to describe the way instability is set up in the system, but not to predict the final state to which the unstable system will tend. This would require a treatment of the non-linear terms, which is a difficult problem.

Within the framework of linear stability it will be sufficient to study the behaviour of the local potential Φ (eq. 2.13) for short times only,[12,13] i.e. immediately after the establishment of the random perturbation $\varepsilon(t)$. We can get this short time behaviour by expanding Φ around $T = 0$ and by retaining only the first few coefficients:

$$\Phi(t) = t\left(\frac{\partial\Phi}{\partial t}\right)_{t=0} + \frac{t^2}{2}\left(\frac{\partial^2\Phi}{\partial t^2}\right)_{t=0} + \frac{t^3}{6}\left(\frac{\partial^3\Phi}{\partial t^3}\right)_{t=0} + \frac{t^4}{24}\left(\frac{\partial^4\Phi}{\partial t^4}\right)_{t=0}$$
$$+ \ldots = t\Phi_1 + \frac{t^2}{2}\Phi_2 + \frac{t^3}{6}\Phi_3 + \frac{t^4}{24}\Phi_4 + \ldots . \tag{4.13}$$

In this linear approximation it is consistent to restrict attention to the following perturbation functions:

$$\varepsilon(t) = \phi(e^{\omega t} - 1) \tag{4.14a}$$

and similarly

$$\bar{\varepsilon}(t) = \bar{\phi}(e^{\varpi t} - 1) \tag{4.14b}$$

where ϕ is an infinitesimal quantity.

From eqs. (4.11) to (4.14) we see that the system will be stable provided

$$\text{Re } \omega < 0. \tag{4.15}$$

Indeed the final state (for $t \to \infty$) will then differ from the initial one by the function ϕ, which is assumed to be an infinitesimal quantity.

We now replace the functions (4.11, 4.12, and 4.14) into eqs. (4.13) and (2.13).*

For $\log f$ we take

$$\log f = \log f_0 + \frac{\varepsilon(t)}{f_0} - \frac{\varepsilon^2(t)}{2f_0^2} + \ldots \tag{4.16a}$$

and

$$\log \bar{f} = \log f_0 + \frac{\bar{\varepsilon}(t)}{f_0} - \frac{\bar{\varepsilon}^2(t)}{2f_0^2} + \ldots . \tag{4.16b}$$

Here we neglect higher-order terms in $\varepsilon(t)$, in agreement with our assumption that ε is an infinitesimal quantity (linear theory).

The subsequent calculations are standard but rather long and we shall not reproduce them here (see ref. 20) for details). We shall merely quote the results and then establish a sufficient condition for the system to be stable. We find (see eq. 4.13) that: (*a*) $\Phi_1 = 0$ identically. (*b*) In Φ_2 no contribution resulting from the collision integral subsists; (*c*) The term Φ_3 gives a first combination of free flow and collision effects in the form

$$\begin{aligned}
\Phi_3(\omega, \bar{\omega}, \phi, \bar{\phi}) = \int d\mathbf{x}\, d\mathbf{v} \Big\{ & (2\omega\bar{\omega}^2 + \omega^2\bar{\omega}) \frac{\phi\bar{\phi}}{f_0} - \omega^2\bar{\omega} \frac{\phi^2\bar{\phi}}{f_0} \\
& + 2\omega \left(\mathbf{F} \frac{\partial\bar{\phi}\bar{\omega}}{\partial\mathbf{v}} \frac{\phi}{f_0} + \mathbf{v} \frac{\partial\bar{\phi}\bar{\omega}}{\partial\mathbf{x}} \frac{\phi}{f_0} \right) \\
& + \frac{4\pi^4\lambda^2 n}{m} \int d\mathbf{v}' \int d\mathbf{l}\, |V_l|^2 \delta(\mathbf{l}\dot{\mathbf{g}}) f_0 f_0' \left[\left(\frac{\partial}{\partial\mathbf{p}} - \frac{\partial}{\partial\mathbf{p}'} \right) \mathbf{l} \left(\frac{\phi\omega}{f_0} + \frac{\phi'\omega'}{f_0'} \right) \right]^2 \\
& - \frac{8\pi^4\lambda^2 n}{m} \int d\mathbf{v}' \int d\mathbf{l}\, |V_l|^2 f_0 f_0' \mathbf{l} \frac{\partial}{\partial\mathbf{v}} \delta(\mathbf{l}\dot{\mathbf{g}}) \left(\frac{\bar{\phi}\bar{\omega}}{f_0} + \frac{\bar{\phi}'\bar{\omega}'}{f_0'} \right) \\
& \times l \left(\frac{\partial}{\partial\mathbf{p}} - \frac{\partial}{\partial\mathbf{p}'} \right) \left(\frac{\phi\omega}{f_0} + \frac{\phi'\omega'}{f_0'} \right) \Big\} + B(\bar{\omega}, \bar{\phi}),
\end{aligned} \tag{4.17}$$

where we did not write explicitly the terms not containing ϕ or ω

* We again take the Landau equation to illustrate our calculations.

(indeed such terms do not contribute to the variational equations deriving from Φ_3).

It is worth noting that the second term in the bracket in eq. (4.17) represents a higher-order contribution in ϕ than the remaining terms which all are of order ϕ^2. This contribution represents a first non-linear effect, which we shall neglect here since we are following a linear-stability approach. In any case, we shall verify that it does not contribute to the equations of neutral stability that we derive below.

(*d*) Finally the term Φ_4 in the development (4.13) of the local potential turns out to be of order ϕ^3. All terms next to Φ_3 therefore contribute to the non-linear effects which we are not considering here.

Let us now analyze in detail the information contained in the functional (4.17). Since $f = f(\phi, \omega)$, the self-consistent eq. (2.16) is replaced by the two equations:

$$\delta\Phi_3/\delta\omega \,\Big|\, \begin{matrix} \omega = \bar{\omega} = 0 \\ \phi = \bar{\phi} \end{matrix} \tag{4.18}$$

and

$$\delta\Phi_3/\delta\phi \,\Big|\, \begin{matrix} \omega = \bar{\omega} = 0. \\ \phi = \bar{\phi} \end{matrix} \tag{4.19}$$

In writing eq. (4.18) explicitly we shall make a further assumption. We shall assume that the frequency ω is a parameter independent of velocity and space. This, of course, is a rather severe restriction since there is no reason for particles of different velocities and positions to respond in an identical way to a random disturbance. We know, for example, that the slow particles are well represented by quasi-steady-state normal solutions of the kinetic equation, whereas for the fast particles the collisions are practically ineffective for building a normal state. Such particles are represented by completely different classes of solution of the kinetic equation,[34,35] which are almost always unstable. If, however, we are only interested in deducing overall conditions of stability for the system as a whole, we may expect that an averaging over all particles, corresponding to a constant-response frequency ω, will give a fairly reasonable result. We shall therefore pursue our analysis by keeping ω independent of $\mathbf{x}$ and $\mathbf{v}$ and postpone till the last Section some remarks concerning a more consistent treatment of the different groups of particle in the system.

When ω is independent of $\mathbf{x}$ and $\mathbf{v}$, eq. (4.18) contains simply a partial derivative with respect to ω which can be evaluated explicitly by using eq. (4.17). The result is

$$\int d\mathbf{x}\, d\mathbf{v}\, 2\omega \frac{\phi^2}{f_0} = \int d\mathbf{x}\, d\mathbf{v} \left\{ -\mathbf{F} \frac{\partial \phi}{\partial \mathbf{v}} \cdot \frac{\phi}{f_0} - \mathbf{v} \frac{\partial \phi}{\partial \mathbf{x}} \cdot \frac{\phi}{f_0} + \frac{8\pi^4 \lambda^2 n}{m} \int d\mathbf{v}' \int d\mathbf{l}\, |V_l|^2 f_0 f_0' \frac{\phi}{f_0} \mathbf{l} \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'} \right) \delta(\mathbf{lg}) \times \mathbf{l} \left(\frac{\partial}{\partial \mathbf{p}} - \frac{\partial}{\partial \mathbf{p}'} \right) \left(\frac{\phi}{f_0} + \frac{\phi'}{f_0'} \right) \right\}. \quad (4.20)$$

This equation provides a relation connecting a term linear in the frequency ω and a term containing the average, taken over space and velocity, of the difference between a dissipative and a convective part. Using the definition eq. (2.23) of entropy and the expressions (4.11) to (4.14) for the distribution functions, we can give to eq. (4.20) an even more precise physical interpretation.* Indeed, the left-hand side is seen to be related to the variation of the time derivative of entropy at time zero, the difference being taken between the states f and f_0. Equation (4.20) expresses this entropy production as a balance between convective terms (first two terms in the right-hand side) and dissipative terms (last term in the right-hand side). When the contribution of the convective terms tend to dominate over the contribution of dissipative terms, we may expect that the system will become unstable and the frequency ω will change sign and become positive.† Equation (4.20) therefore provides a stability con-

* This remark is due to Dr. W. Strieder.

† It is easily verified that the sign of ω due only to collisions is never positive, provided that $f_0 f_0'$ commutes with $\delta(\mathbf{lg})\mathbf{l}\left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'}\right)$:

$$\omega_{col}^2 \int d\mathbf{v} \frac{\phi^2}{f_0} = \frac{4n^4\lambda^2 n}{m^2} \int d\mathbf{v}\, d\mathbf{v}' \int d\mathbf{x} \int d\mathbf{l}\, |V_l|^2 f_0 f_0' \left(\frac{\phi}{f_0} + \frac{\phi'}{f_0'} \right) \mathbf{l} \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'} \right) \times \delta(\mathbf{lg}) \mathbf{l} \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'} \right) \left(\frac{\phi}{f_0} + \frac{\phi'}{f_0'} \right)$$

$$= \frac{-4n^2\lambda^2 n}{m^2} \int d\mathbf{x} \int d\mathbf{v}\, d\mathbf{v}' \int d\mathbf{l} |V_l|^2 \delta(\mathbf{lg}) f_0 f_0' \times \left[\mathbf{l} \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'} \right) \left(\frac{\phi}{f_0} + \frac{\phi'}{f_0'} \right) \right]^2.$$

dition, expressing the existence of a marginal state[33] characterized by the fact that $\omega = 0$. Such marginal states are known to exist whenever the external constraints do not depend on time.* Equation (4.20) thus becomes

$$\int d\mathbf{x}\, d\mathbf{v} \left[\mathbf{F} \frac{\partial \phi}{\partial \mathbf{v}} \frac{\phi}{f_0} + \mathbf{v} \frac{\partial \phi}{\partial \mathbf{x}} \frac{\phi}{f_0} \right] = \int d\mathbf{x}\, d\mathbf{v}\, d\mathbf{v}' \frac{8\pi^4 \lambda^2 n}{m} \int d\mathbf{l}\, |V_l|^2 \times f_0 f_0' \frac{\phi}{f_0} \mathbf{l} \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'} \right) \delta(\mathbf{lg}) \mathbf{l} \left(\frac{\partial}{\partial \mathbf{p}} - \frac{\partial}{\partial \mathbf{p}'} \right) \left(\frac{\phi}{f_0} + \frac{\phi'}{f_0'} \right). \quad (4.21)$$

For given functions ϕ, eq. (4.21) provides a value $\mathbf{F}_c$ for the critical field as a function of thermal gradient, density, mass, temperature, etc. It should be realized, however, that the functions ϕ and $\bar{\phi}$ are among the unknowns of the problem and they are to be specified from eq. (4.19). Therefore, eq. (4.21) in itself does not yield the complete answer about the conditions for stability of the system. We have to determine first the function ϕ from eq. (4.19) and then insert it into eq. (4.21) to find an equation relating field and thermal gradient. In some cases the form of the function ϕ is easily guessed, and eq. (4.21) can by itself provide much of the information relevant to stability.[20] In general, however, one has to use eq. (4.19). We shall now show that this equation can also provide a compact stability criterion.

It is convenient to parametrize the function ϕ by expanding it in terms of a complete set of orthogonal functions u_i:

$$\phi = \sum_i a_i u_i(\mathbf{x}, \mathbf{v}) \quad (4.22a)$$

and similarly

$$\bar{\phi} = \sum_i \bar{a}_i u_i(\mathbf{x}, \mathbf{v}). \quad (4.22b)$$

Equation (4.19) is then replaced by the set of equations

$$\left. \frac{\partial \Phi_3}{\partial a_i} \right|_{\substack{a_i = \bar{a}_i \\ \omega = \bar{\omega}}} = 0 \qquad (i = 1, 2, \ldots, n \ldots). \quad (4.23)$$

* This statement is always true in hydrodynamics. It is also explicitly verified in the example of Section 5. In the most general case, however, some reserve should be attached to a statement that the marginal state always corresponds to a stable–unstable transition. Such could, e.g., be the case for systems exhibiting wave-type solutions (plasma waves, etc.) or for systems with field- and space-dependent collision operators.

When truncated at a finite $n \geqq i$, this is a system of n algebraic homogenous equations with n unknowns. If the term of third order in ϕ is neglected in eq. (4.17) for Φ_3, the system is in addition a linear homogeneous system. The secular equation of this system, expressing the existence of non-vanishing perturbation amplitudes ϕ, yields an equation

$$A(\omega, |\mathbf{F}|, \gamma) = 0 \tag{4.24}$$

relating frequency ω, external field $|\mathbf{E}|$ and thermal gradient γ (and, of course, temperature, mass, and density as well). The same equation for the marginal state yields

$$A_0(|\mathbf{F}|, \gamma) = 0. \tag{4.25}$$

The roots of this equation give then a value of the critical field and/or the critical gradient, above which the system becomes unstable. This equation therefore provides a new stability condition.

In the next Section we shall write eq. (4.25) in a specific example and see how the different physical parameters appear. We conclude this paragraph by noticing that the cubic term in ϕ in the eq. (4.17) for Φ_3 does not contribute to eq. (4.25), in the same way as all other terms of third order in ω and $\bar{\omega}$. In the linear stability approximation the critical values are therefore consistently given by eq. (4.25), whereas the first non-linear correction to these values would come from the term Φ_4 in the expansion (4.13) of the local potential.

5. APPLICATIONS TO SIMPLE STABILITY PROBLEMS

We shall now sketch an application of the secular eq. (4.25) in the case of a homogeneous system ($\gamma = 0$) subject to an external force per unit mass, $\mathbf{F}$. More specifically we shall consider the well-known plasma runaway problem[36] within the framework of our variational approach. The electron runaway effect, i.e. the continuous acceleration of electrons in a plasma in a strong electric field, has been discussed in much detail by several authors.[34–36] One considers a two-component (electron–ion) plasma and demonstrates that there exists a critical value of the electric field beyond which the electron distribution itself, or one of its moments (e.g.

the electric current) grows exponentially in time. Qualitatively one can say that in this case the acceleration due to the electric field dominates the dissipative effects due to electron–electron and, mainly,[36] to electron–ion collisions.

In order to describe this problem meaningfully within the framework of the local potential it is necessary to consider a Landau equation for the two-component system of electrons and ions. We have also to introduce the Debye screening due to the long-range Coulomb interaction. When all this is taken into account it is shown[22] that the electron collision operator can be written in the form:

$$\psi = \psi_{ee} + \psi_{ei}$$
$$= \frac{2\pi e^4}{m_e} \log \frac{\Lambda}{\kappa} \left[n_e \int \mathrm{d}\mathbf{v}' \frac{1}{g^3} \frac{\partial}{\partial v_r} (g^2 \delta_{rs} - g_r g_s) \frac{1}{m_e} \left(\frac{\partial}{\partial v_s(e)} - \frac{\partial}{\partial v_s'(e)} \right) \right.$$
$$\left. + n_i \int \mathrm{d}\mathbf{v}' \frac{1}{g^3} \frac{\partial}{\partial v_r} (g^2 \delta_{rs} - g_r g_s) \left(\frac{1}{m_e} \frac{\partial}{\partial v_s(e)} - \frac{1}{m_i} \frac{\partial}{\partial v_s'(i)} \right) \right] \quad (5.1)$$

The indices e and i refer to electrons and ions, respectively. Here e is the electronic charge, κ the inverse of the Debye length, and Λ the cut-off for the close collisions. Repeated indices are summed over. All other symbols have already been introduced in Section 2.

In order to calculate eq. (4.25) we have to specify a little more the form (4.22) of the function ϕ. In the present example we shall truncate the expansion (4.22) in the second term and use the form

$$\phi = a_0 \phi_0 + a_1 \phi_1 \quad (5.2a)$$

or what will be more convenient

$$\phi = \phi_0 (a_0 + a_1 S_{3/2}^{(i)}) = \phi_0 (a_0 + a_1 S) \quad (5.2b)$$

S being the first Sonine polynomial.[21] The function ϕ_0 will be specified below, but for the moment we can proceed using a general form for it. To simplify the calculations, we shall also neglect the effect of electron–electron collisions in the Landau equation. This is a very reasonable assumption since it is known[36] that most of the Joule heating in the plasma comes from the electron–ion collisions. The assumption may break down for the very fast electrons.[34] As we are interested in the overall stability

of the system, we do not consider the effect of fast electrons here.

We now insert the expressions (5.1) and (5.2) into (4.17). The secular eq. (4.25) takes the form:*

$$\det \|a_{ij}\| = 0, \tag{5.3}$$

where the coefficients a_{ij} depend on the field, the quasi-stead-state function f_0 and the ion–electron interaction. Their explicit form is[37] (we recall that the system is homogeneous):

$$a_{11} = \frac{2e\mathbf{E}}{m_e} \int \mathrm{d}\mathbf{v} \, \frac{\phi}{f_0} \frac{\partial \phi_0}{\partial \mathbf{v}} - \int \mathrm{d}\mathbf{v} \, \mathrm{d}\mathbf{v}' \, \phi_0 f_0' \frac{\partial}{\partial \mathbf{v}} [\phi_0, \phi_0'] \tag{5.4a}$$

$$a_{12} = \frac{2e\mathbf{E}}{m_e} \int \mathrm{d}\mathbf{v} \, \frac{\phi}{f_0} \frac{\partial \phi_0 S}{\partial \mathbf{v}} - \int \mathrm{d}\mathbf{v} \, \mathrm{d}\mathbf{v}' \, \phi_0 S f_0' \frac{\partial}{\partial \mathbf{v}} [\phi_0 \phi_0'] \tag{5.4b}$$

$$a_{21} = \frac{2e\mathbf{E}}{m_e} \int \mathrm{d}\mathbf{v} \, \frac{\phi_0 S}{f_0} \frac{\partial \phi_0}{\partial \mathbf{v}} - \int \mathrm{d}\mathbf{v} \, \mathrm{d}\mathbf{v}' \, \phi_0 f_0' \frac{\partial}{\partial \mathbf{v}} [\phi_0 S, \phi_0' S'] \tag{5.4c}$$

$$a_{22} = \frac{2e\mathbf{E}}{m_e} \int \mathrm{d}\mathbf{v} \, \frac{\phi_0 S}{f_0} \frac{\partial \phi_0 S}{\partial \mathbf{v}} - \int \mathrm{d}\mathbf{v} \, \mathrm{d}\mathbf{v}' \, \phi_0 S f_0' \frac{\partial}{\partial \mathbf{v}} [\phi_0 S, \phi_0' S'], \tag{5.4d}$$

where we have

$$[A, A] = \frac{16\pi^4 e^4 n_i}{m_e} \int \mathrm{d}\mathbf{l} \, |\mathrm{V}_l|^2 \mathbf{l} \, \delta(\mathbf{l}\mathbf{g})\mathbf{l} \left(\frac{1}{m_e} \frac{\partial}{\partial \mathbf{v}} - \frac{1}{m_i} \frac{\partial}{\partial \mathbf{v}} \right) \left(\frac{A}{f_0} + \frac{A'}{f_0'} \right). \tag{5.5}$$

In order to evaluate eq. (5.3) explicitly we still have to take a specific form for the stead-state function f_0 and chose a trial form for the part ϕ_0 of the perturbation (see eq. 5.2). We shall take the usual form of f_0 linear in the field:[21]

$$f_0(e) = n_e \left(\frac{m_e}{2\pi k T_e} \right)^{3/2} \left[1 + \tau \frac{\mathrm{e}\mathbf{E}}{k T_e} \mathbf{v} \right] \exp \left[- \frac{m_e \mathbf{v}^2}{2 k T_e} \right]. \tag{5.6}$$

The relaxation time τ, generally velocity-dependent, will be here approximated by:[21]

$$\tau = \frac{m_e m_i}{e^2 \rho} \cdot \sigma. \tag{5.7}$$

* It has been verified that in the absence of electric field the secular equation always predicts $\omega < 0$, i.e. that the system is stable.

In the above formulae ρ is the total mass density, and σ is the first approximation to the electrical conductivity coefficient.[21]

Finally we shall limit ourselves to the following simple form for ϕ_0,

$$\phi_0(e) = n_e \left(\frac{m_e}{2\pi k T_e}\right)^{3/2} \exp\left(-\frac{m_e v^2}{2kT_e}\right) \frac{m_e \mathbf{v}}{2kT_e} \mathbf{u}, \tag{5.8}$$

$\mathbf{u}$ being a (infinitesimal) perturbation to the steady-state current.

We can now evaluate explicitly the determinant in eq. (5.3). To simplify the calculations we have taken a Lorentz plasma (sero-temperature ions).[21] Relation (5.3) gives in this case a transcendental equation for the field, E. Detailed numerical calculations have been carried out.[37] In the special case one takes $a_1 = 0$ in eq. (5.2); the result reads

$$E_0 = 0{\cdot}2 \times \frac{n_i e^3 \log \Lambda/K}{8\pi k T}. \tag{5.9}$$

independently of any estimate of the parameter $\mathbf{u}$ appearing in eq. (5.8).[36] The result in eq. (5.10) agrees well with Dreicer's result. However, one should appreciate that our result has been derived from a consistent analysis of the linear stability of the distribution function itself and not of its moments. In our opinion, this method could be used to study several other plasma stability problems from a unified point of view.

6. DISCUSSION AND CONCLUDING REMARKS

In this study we have developed some of the fundamental properties of the local potential as a means of generating kinetic equations and studying their steady-state solutions and stability properties. In particular, the approach to the stability problem outlined in the last two Sections is promising for the study of specific problems by local-potential methods. We should not neglect to stress, however, that although the general approach sketched in Section 4 seems to be always possible, the discussion of specific examples meets several practical difficulties. For instance, we had to simplify considerably the model discussed in Section 5 in order to deduce the stability condition in a fairly straightforward way. The most severe of these simplifications has been the use of functions (5.6) and (5.8) to describe the steady

state and the pertubation amplitude, respectively. These forms are known to describe very well the hydrodynamic behaviour of a system[21,24] where collisions are the dominant mechanism giving rise to the different transport properties. Relatively slow particles, for which the collision cross-section is appreciable, may reasonably be expected to exhibit a hydrodynamic behaviour. They could thus be well described by the Chapman–Enskog-like forms (5.6) and (5.8).[21,24] On the other hand, fast particles undergo a very weak diffusion process in velocity space and their distribution function should considerably deviate from the forms (5.6) and (5.8). In order to determine this function one has to solve the equation to which the Landau equation reduces in the domain of high velocities,[34,35] and this problem is still unsolved from many points of view. In any case the response frequency ω introduced in Section 4 will assume at least two values, ω_1 for the slow particles and ω_2 for the fast particles. One would expect that even for weak fields ω_2 will be positive and that fast particles will run away. The system as a whole will become unstable when a moment of the distribution function acquires a positive frequency. In general, this frequency, ω will be a function of the field via the frequencies ω_1 and ω_2:

$$\omega = \omega[\omega_1(E), \quad \omega_2(E)]. \tag{6.1}$$

The overall stability properties of the system result, therefore, from the competition between the stabilizing effect of slow particles and the instabilities induced by the run-away particles. Such a treatment should predict a lower value for the critical run-away field since now a part of the particles no longer play a stabilizing role. An approach to the run-away problem following these lines is under investigation.

Another interesting question not considered in the present study is the use of the methods developed here to study several kinds of hydrodynamic instability from the statistical-mechanical point of view. Such a problem can be separated in two parts: One may consider the case where the perturbed solutions of the kinetic equation remain normal (e.g., Chapman–Enskog) solutions,[21,24] i.e. they are perturbed through the changes of hydrodynamic parameters such as density, temperature, or average velocity. These quantities satisfy the hydrodynamic equations

that exhibit certain types of unstable solution.[33] The same instabilities should then be reflected in the form of the distribution function. The converse, however, is not always true; one can say rather that the instabilities of the kinetic equation reduce to the hydrodynamic instabilities for certain classes of perturbation.[38] The second possible question refers to a perturbation which changes the normal state itself, e.g. to a rapidly varying state explicitly dependent on time. In this case the normal solutions themselves are unstable and one deviates from the hydrodynamic regime. This should be the case for fast particles, for which the collisions are ineffective. The effect of such fast particles could become appreciable in very dilute systems* under a strong gradient or under a high-frequency external disturbance. *A priori* such an instability should take place at a later stage than the unstable hydrodynamic transition. It will at the same time determine the limits of validity of the hydrodynamic equations.

It is to be expected that further investigation of these "microscopic instability" problems will lead to further elucidation of the role of the local potential in stability theory and possibly indicate some new applications of the Galerkin and the Lyapounoff method.

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APPENDIX A

The Local Potential for the Boltzmann and for the Balescu-Lenard Operator

We shall briefly discuss here the case when one uses in the kinetic equation the Boltzmann[21] or the Balescu–Lenard[22] form for the collision operator ψ,

$$B = \int d\mathbf{v}_1 \, d\mathbf{k} \, w(\mathbf{k}|\mathbf{k}') |\mathbf{g}| (f'f_1' - ff_1) \tag{A.1}$$

* The range of density could be, e.g. intermediate between the extreme Knudsen and the usual hydrodynamic domain.

and

$$R = \frac{8\pi^4 e^4 n}{m^2} \int d\mathbf{v}' \int d\mathbf{l}\, |V_l|^2 \frac{\partial}{\partial \mathbf{v}} \frac{1}{|\varepsilon(\mathbf{v}; f)|^2} \delta(\mathbf{lg}) \mathbf{l} \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'} \right) ff', \tag{A.2}$$

respectively. We consider here a one-component system. In eq. (A.1) w is the collision cross-section, and the primes indicate the values of the distribution functions for velocities after the direct collision. $d\mathbf{k}$ denotes an integration over the unit sphere and $\mathbf{k}$ a vector in the direction of $\mathbf{g}$. In eq. (A.2) ε is the dielectric constant,

$$\varepsilon(\mathbf{v}; f) = 1 + \lim_{\varepsilon \to 0} 2\pi^4 \omega_p^2 V_l \int d\mathbf{v}_1 \frac{\mathbf{l}[\partial / \partial \mathbf{v}_1] - f(\mathbf{v}_1)}{\mathbf{l}(\mathbf{v} - \mathbf{v}_1) - i\varepsilon} \tag{A.3}$$

ω_p being the plasma frequency.[22]

Since the convection terms remain the same as in eq. (2.13) we shall evaluate only the collisional parts of the local potential. Following the same line as in Section 2 we have:[20]

$$\begin{aligned} \Delta \Phi_{\text{col}}^B &= -\int_0^T dt \int d\mathbf{x}\, d\mathbf{v}\, d\mathbf{v}_1\, d\mathbf{k}\, w|\mathbf{g}|(f'f_1' - ff_1)\, \Delta \log f \\ &= -\frac{1}{2} \int_0^T dt \int d\mathbf{x}\, d\mathbf{v}\, d\mathbf{v}_1\, d\mathbf{k}\, w|\mathbf{g}|(f'f_1' - ff_1)\, \Delta \log ff_1 \\ &= -\frac{1}{4} \int_0^T dt \int d\mathbf{x}\, d\mathbf{v}\, d\mathbf{v}_1\, d\mathbf{k}\, w|\mathbf{g}| ff_1 \left(1 - \frac{f'f_1'}{ff_1} \right) \Delta \log \frac{f'f_1'}{ff_1}. \end{aligned} \tag{A.4}$$

Applying the idea of local potential and dropping the fluctuation of f's in the product ff_1 following the factor $w|\mathbf{g}|$, we may integrate (A.4) and get

$$\Phi_{\text{col}}^B = -\frac{1}{4} \int_0^T dt \int d\mathbf{x}\, d\mathbf{v}\, d\mathbf{v}_1\, d\mathbf{k}\, w|\mathbf{g}| \tilde{f}\tilde{f}_1 \left(1 - \frac{f'f_1'}{ff_1} + \log \frac{f'f_1'}{ff_1} \right). \tag{A.5}$$

Similarly we have:

$$\frac{m^2}{8\pi^4 e^4 n}\,\Delta\Phi^R_{\mathrm{col}} = -\int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{v}\,\mathrm{d}\mathbf{v}'\,\mathrm{d}\mathbf{l}\,|V_l|^2 \Delta \log f \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'}\right)$$
$$\times \mathbf{l}\,\frac{1}{|\varepsilon(\mathbf{v};f)|^2}\,\delta(\mathbf{lg})\mathbf{l}\left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'}\right) ff'$$
$$= \frac{1}{2}\int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{v}\,\mathrm{d}\mathbf{v}'\,\mathrm{d}\mathbf{l}\,|V_l|^2 \left[l\left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'}\right)\Delta \log ff'\right]$$
$$\times\,\delta(\mathbf{lg})\,\frac{ff'}{|\varepsilon(\mathbf{v};f)|^2}\left[\mathbf{l}\left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'}\right)\log ff'\right] \qquad \text{(A.6)}$$

and

$$\Phi^R_{\mathrm{col}} = \frac{2\pi^4 e^4 n}{m^2}\int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{v}\,\mathrm{d}\mathbf{v}'\,\mathrm{d}\mathbf{l}\,|V_l|^2\,\frac{\bar{f}\bar{f}'}{|\varepsilon(\mathbf{v};\bar{f})|^2}\,\delta(\mathbf{lg})$$
$$\times\left[\mathbf{l}\left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'}\right)\log ff'\right]^2. \qquad \text{(A.7)}$$

Again in going from eq. (A.6) to (A.7) we did not take into account the fluctuations of the quantity $ff'/|\varepsilon(\mathbf{v};f)|^2$. It is seen that both Φ^B_{col} and Φ^R_{col} are positive semi-definite quantities. Moreover, it is verified that the convective terms remove the terms linear in Δf in (A.5) and (A.7), in the same way as in Section 2. The minimum property expressed by eq. (2.18) is therefore again fulfilled.

APPENDIX B

Local Potential and Detailed Balance

In deriving expressions (2.13), (A.5), and (A.7) for the local potential, we have used the symmetry properties of the collision operator. In this Appendix we stress that the procedure is easily extended to cover cases where no detailed balance holds for the cross-section in eq. (A.1). We also study the case where the presence of a high-frequency external field modifies the propagator in eq. (2.13) to a δ-$(\mathbf{lg} + \omega)$ function, ω being the frequency of

* The problem discussed here was brought up during discussions with Prof. P. Résibois.

the field. Our remarks hold only for classical kinetic equations. In the quantum case some supplementary difficulties are introduced and our proof below cannot be applied.*

Consider first the Boltzmann equation where detailed balance holds in a generalized form:[18,39]

$$\sum_{kl} \int \mathrm{d}\mathbf{v}' \, \mathrm{d}\mathbf{v}_1' \, w(ij|kl) = \sum_{kl} \int \mathrm{d}\mathbf{v}' \, \mathrm{d}\mathbf{v}_1' \, w(kl|ij). \tag{B.1}$$

In this case the Boltzmann operator (A.1) reads[18]

$$B = \sum_{jkl} \int \mathrm{d}\mathbf{v}_1 \, \mathrm{d}\mathbf{v}' \, \mathrm{d}\mathbf{v}_1' \, |\mathbf{g}| [f_k' f_l' w(kl|ij) - f_i f_j w(ij|kl)]. \tag{B.2}$$

Multiplying by $-\int_0^T \mathrm{d}t \sum_i \int \mathrm{d}\mathbf{v} \, \Delta \log f_i$ and using (B.1) yields

$$\Delta\Phi = -\int_0^T \mathrm{d}t \sum_{ijkl} \int \mathrm{d}\mathbf{v} \, \mathrm{d}\mathbf{v}_1 \, \mathrm{d}\mathbf{v}' \, \mathrm{d}\mathbf{v}_1' \, \Delta \log f_1 (f_k' f_l' - f_i f_j) w(kl|ij) |\mathbf{g}|. \tag{B.3}$$

This has the same form as the first line in eq. (A.4). We may therefore apply step by step the derivation of Appendix A to yield an expression similar to (A.5).

Let us consider next the Landau operator with a frequency dependent propagator:

$$\int \mathrm{d}\mathbf{v}' \, \mathrm{d}\mathbf{l} \, |V_l|^2 \mathbf{l} \frac{\partial}{\partial \mathbf{v}} \delta_-(\mathbf{l}\mathbf{g} + \omega) \mathbf{l} \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'} \right) f f'$$

Multiplying by $-\int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{v} \, \Delta \log f$ we obtain

$$\Delta\Phi_{\mathrm{col}}^L(w) = -\int_0^T \mathrm{d}t \int \mathrm{d}\mathbf{v} \, \mathrm{d}\mathbf{v}' \, \mathrm{d}\mathbf{l} \, |V_l|^2 \, \Delta \log f \, \mathbf{l} \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'} \right) \times \delta_-(\mathbf{l}\mathbf{g} + \omega) \mathbf{l} \left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'} \right) f f'. \tag{B.4}$$

In this integrand we change variables:

$$\mathbf{v} \leftrightarrow \mathbf{v}'; \quad \mathbf{l} \to -\mathbf{l}.$$

* P. Résibois, personal communication.

The function $\delta_-(\mathbf{lg} + \omega)$ remains unchanged and we obtain

$$\Delta\Phi^L_{\text{col}}(w) = -\frac{1}{2}\int_0^T dt \int d\mathbf{v}\, d\mathbf{v}'\, d\mathbf{l}\, |V_l|^2\, \Delta \log ff' \times \mathbf{l}\left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'}\right) ff' \delta_-(\mathbf{lg} + w)\mathbf{l}\left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'}\right) \log ff', \tag{B.5}$$

or finally

$$\Phi^L_{\text{col}}(\omega) = \frac{1}{4}\int_0^T dt \int d\mathbf{v}\, d\mathbf{v}'\, d\mathbf{l}\, |V_l|^2 \bar{f}\bar{f}' \delta_-(\mathbf{lg} + w) \times \left[\mathbf{l}\left(\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'}\right) \log ff'\right]^2 \tag{B.6}$$

This has the same form as the collisional part of the local potential in eq. (2.13).

APPENDIX C

Convergence of the Iteration Procedure

Here we shall prove that the iterative solution of the equation derived from the local potential (3.15) may lead to a convergent procedure. In this way we shall generalize Kruskal's proof[11] of convergence of the iterative solution of the heat equation.

The equation generating the iterative procedure is (see eq. 3.16):

$$F\frac{\partial \bar{f}}{\partial v} - \frac{\zeta kT}{m}\frac{\partial}{\partial v} f_e \frac{\partial}{\partial v}\frac{f}{f_e} = 0. \tag{C.1}$$

Let us put

$$f = f_0 + u \tag{C.2a}$$

and

$$\bar{f} = f_0 + \bar{u}, \tag{C.2b}$$

f_0 being an exact solution of eq. (C.1). It follows that

$$F\frac{\partial \bar{u}}{\partial v} - \frac{\zeta kT}{m}\frac{\partial}{\partial v} f_e \frac{\partial}{\partial v}\frac{u}{f_e} = 0. \tag{C.3}$$

It is clear that the convergence will be established whenever we can prove that

$$\|u\| < \|\bar{u}\|, \tag{C.4}$$

where we defined $$\|u\| = \left(\int \mathrm{d}v |u|^2\right)^{1/2}. \tag{C.5a}$$

Indeed the first iteration of eq. (C.3) will then lead to a function $f = f_0 + u$ which is closer to f_0 than the first estimation $\bar{f} = f_0 + \bar{u}$, and so on.

In order to investigate under what conditions eq. (C.4) is true we first write

$$u = \sigma f_e \tag{C.6}$$

The equation becomes

$$F \frac{\partial \bar{\sigma} f_e}{\partial v} - \frac{\zeta k T}{m} \frac{\partial}{\partial v} f_e \frac{\partial}{\partial v} \sigma = 0; \tag{C.7}$$

and for the convergence it will be sufficient to prove that

$$\|f_e^{1/2} \sigma\| < \|f_e^{1/2} \bar{\sigma}\|. \tag{C.8}$$

Equation (C.7) leads to the formal solution

$$\sigma(\xi) = \frac{F}{\zeta} \left(\frac{m}{kT}\right)^{1/2} \frac{1}{\frac{\partial}{\partial \xi} f_e(\xi) \frac{\partial}{\partial \xi}} \frac{\partial \bar{\sigma} f_e(\xi)}{\partial \xi}, \tag{C.9}$$

where we used the reduced variable

$$\xi = (m/kT)^{1/2} v. \tag{C.10}$$

In order to estimate the inverse of the Fokker–Planck operator let us study the eigenvalue problem for[40]

$$\frac{\partial}{\partial \xi} f_e \frac{\partial}{\partial \xi} = \exp\left(-\tfrac{1}{2}\xi^2\right) \left(\frac{\mathrm{d}^2}{\mathrm{d}\xi^2} - \xi \frac{\mathrm{d}}{\mathrm{d}\xi}\right). \tag{C.11}$$

We first study the eigenvalue problem

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\xi^2} - \xi \frac{\mathrm{d}}{\mathrm{d}\xi}\right) u_n = \lambda_n u_n. \tag{C.12}$$

It is recognized[29] that

$$u_n = H_n(\xi/\sqrt{2}) \tag{C.13a}$$

and $$\lambda_n = -n, \tag{C.13b}$$

H_n being the Hermite polynomials.

Let us now develop the function $\partial\bar{\sigma}f_e/\partial\xi$ in a series of these polynomials weighted by $f_e = \exp(-\frac{1}{2}\xi^2)$:

$$\frac{\partial\bar{\sigma}f_e}{\partial\xi} = \sum_{n=1}^{\infty} a_n f_e H_n(\xi/\sqrt{2})$$

$$= \sum_n \frac{1}{\sqrt{2N_n}} \left(\int_{-\infty}^{\infty} d\xi\, H_n\left(\frac{\xi}{\sqrt{2}}\right)\frac{\partial\bar{\sigma}f_e}{\partial\xi}\right) f_e H_n\left(\frac{\xi}{\sqrt{2}}\right), \quad \text{(C.14)}$$

where we used eq. (3.32).

Now (see eqs. C.12 and C.13)

$$\exp(-\tfrac{1}{2}\xi^2)\left(\frac{d^2}{d\xi^2} - \xi\frac{d}{d\xi}\right) H_n\left(\frac{\xi}{\sqrt{2}}\right) = -n\exp(-\tfrac{1}{2}\xi^2) H_n\left(\frac{\xi}{\sqrt{2}}\right). \quad \text{(C.15)}$$

Or, dividing through by $\exp(-\frac{1}{2}\xi^2)\left(\frac{d^2}{d\xi^2} - \xi\frac{d}{d\xi}\right)$:

$$-\frac{1}{n} H_n\left(\frac{\xi}{\sqrt{2}}\right) = \frac{1}{\exp(-\frac{1}{2}\xi^2)\left(\frac{d^2}{d\xi^2} - \xi\frac{d}{d\xi}\right)} \cdot \exp(-\tfrac{1}{2}\xi^2) \cdot H_n\left(\frac{\xi}{\sqrt{2}}\right). \quad \text{(C.16)}$$

Combining eqs. (C.9), (C.14), and (C.16), we obtain:

$$\sigma(\xi) = -\frac{F}{\zeta}\left(\frac{m}{kT}\right)^{1/2} \sum_{n=1}^{\infty} \frac{1}{\sqrt{2N_n}\, n} \int_{-\infty}^{\infty} d\xi\, H_n \frac{\partial\bar{\sigma}f_e}{\partial\xi} \cdot H_n\left(\frac{\xi}{\sqrt{2}}\right). \quad \text{(C.17)}$$

Multiplying by $\exp(-\frac{1}{4}\xi^2)$ and taking moduli in both sides, we have $\|e^{-\frac{1}{4}\xi^2}\sigma\| =$

$$\frac{F}{\zeta}\left(\frac{m}{kT}\right)^{1/2}\left[\left(\sum_{n=1}^{\infty} \frac{1}{\sqrt{2N_n}\, n}\left(\int_{-\infty}^{\infty} d\xi\, H_n \frac{\partial\bar{\sigma}f_e}{\partial\xi}\right) H_n\left(\frac{\xi}{\sqrt{2}}\right) e^{-1/4\xi^2}\right)^2\right]^{1/2}$$

$$= \frac{F}{\zeta}\left(\frac{m}{kT}\right)^{1/2}\left[\sum_{n=1}^{\infty} \frac{1}{\sqrt{2}\cdot n^2 N_n}\left(\int_{-\infty}^{\infty} d\xi\, H_n\left(\frac{\xi}{\sqrt{2}}\right)\frac{\partial\bar{\sigma}f_e}{\partial\xi}\right)^2\right]^{1/2}, \quad \text{(C.18)}$$

where we used the orthonormality property of Hermite polynomials:

$$\int_{-\infty}^{\infty} d\xi\, H_n\left(\frac{\xi}{\sqrt{2}}\right) H_m\left(\frac{\xi}{\sqrt{2}}\right) e^{-1/2\xi^2} = \sqrt{2N_n}\,\delta nm. \quad \text{(C.19)}$$

Let us now estimate the integral in the right-hand side of eq. (C.18). We have:

$$\left(\int_{-\infty}^{\infty} \mathrm{d}\xi\, H_n\left(\frac{\xi}{\sqrt{2}}\right)\frac{\partial \bar{\sigma} f_e}{\partial \xi}\right)^2 = \left(\int_{-\infty}^{\infty} \mathrm{d}\xi\, \frac{\partial H_n(\xi/\sqrt{2})}{\partial \xi} f_e \bar{\sigma}\right)^2$$

$$= 4n^2\left(\int_{-\infty}^{\infty} \mathrm{d}\xi\, H_{n-1}^2 e^{-1/4\xi^2}(e^{-1/4\xi^2}\bar{\sigma})\right)^2 \qquad \text{(C.20a)}$$

$$\leqq 4n^2 \int_{-\infty}^{\infty} \mathrm{d}\xi\, H_{n-1}^2 e^{-1/4\xi^2} \|e^{-1/4\xi^2}\bar{\sigma}\|^2$$

$$= 4n^2\sqrt{2}\,.\, N_{n-1}\|e^{-1/4\xi^2}\bar{\sigma}^2\|^2 \qquad \text{(C.20b)}$$

Equation (C.18) therefore becomes

$$\|e^{-1/4\xi^2}\sigma\| \leqq \frac{F}{\zeta}\left(\frac{m}{kT}\right)^{1/2}\left(\sum_{n=1}^{\infty}\frac{4N_{n-1}}{N_n}\right)^{1/2}\|e^{-1/4\xi^2}\bar{\sigma}\|$$

$$= \frac{\sqrt{2}F}{\zeta}\left(\frac{m}{kT}\right)^{1/2}\left(\sum_{n=1}^{\infty}\frac{1}{n}\right)^{1/2}\|e^{-1/4\xi^2}\bar{\sigma}\|. \qquad \text{(C.21)}$$

We notice that the sum over n in eq. (C.21) diverges logarithmically. The reason is that in passing from the exact relation (C.20a) to eq. (C.20b) we used the Schwartz inequality which constitutes a rather poor estimation of a scalar product. In the absence of anything better we shall now restrict ourselves to iterative procedures starting fairly close to the exact solution, f_0, of the problem.[11] This means that $\bar{u}/f_0$ is a small quantity which can be approximated by a finite number of terms in a series expansion in Hermite polynomials (see eq. C.14). Therefore the sum in eq. (C.21) effectively runs to a finite number N. We have:

$$\sum_{n=1}^{N}\frac{1}{n} \leqslant C + \log N + \frac{1}{2N},$$

C being the Euler constant, and

$$\|e^{-1/4\xi^2}\sigma\| \leqq \left(\frac{2m}{kT}\right)^{1/2}\frac{F}{\zeta}\left(1 + \log N + \frac{1}{2N}\right)^{1/2}\|e^{-1/4\xi^2}\bar{\sigma}_N\|. \qquad \text{(C.22)}$$

$\bar{\sigma}_N$ is here the approximate first estimation in the iteration procedure. We see that eq. (C.8) is satisfied provided that

$$F < \left(\frac{kT}{2m}\right)^{1/2} \frac{\zeta}{\left(C + \log N + \frac{1}{2N}\right)^{1/2}}. \tag{C.23}$$

Apart from the factor $\left(C + \log N + \frac{1}{2N}\right)^{1/2}$ in the denominator, this condition has the same form as in eq. (3.37). This factor, however, does not introduce any strong dependence of the result upon the number of terms taken in the expansion of $\bar{\sigma}_N$. Indeed we see that when we pass from, e.g., 10 to 100 terms the only difference in the value of F is a factor $\sqrt{2/3}$. Therefore we can say that the convergence condition (C.23) covers a considerably wide range of problems encountered in many physical situations.

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THERMAL DIFFUSION OF HALIDES IN AQUEOUS SOLUTION

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I. INTRODUCTION

The phenomenon of thermal diffusion occurs in physicochemical systems containing more than one component if the temperature distribution is not uniform. It results in a separation, some of the components accumulating in the warmer and others in the cooler regions of the system.

If, in the absence of an external electromagnetic field, dissipation terms of the nature of first-order tensors are retained in the production of entropy σ per unit time and unit volume

$$\sigma = \sum_i J_i X_i \tag{1}$$

then the following well-known relations hold between the heat flux $\boldsymbol{W}$, the mass flux $\rho_\gamma \boldsymbol{\Delta}_\gamma$ of component γ ($\gamma = 1,2, \ldots, c$) with respect to the velocity $\boldsymbol{v}$ of the bulk movement, and the forces $\boldsymbol{\nabla}\mu_\gamma$ (chemical potential gradient) and $\boldsymbol{\nabla}T$ (temperature gradient):

$\rho_\gamma \mathbf{\Delta}_\gamma \sim D\nabla\mu_\gamma$ expresses ordinary diffusion, while $\boldsymbol{W} \sim \lambda\nabla T$ expresses thermal conduction. D is the isothermal diffusion coefficient and λ the thermal conductivity.

The coupling $\rho_\gamma \mathbf{\Delta}_\gamma \sim D'\nabla T$ constitutes thermal diffusion, with the reciprocal coupling (in the sense of the Onsager relations) $\boldsymbol{W} \approx D'\nabla\mu_\gamma$ (the Dufour effect). D' is the thermal diffusion coefficient.

Thermal diffusion is measured as the ration D'/D (the Soret coefficient, s_T) for liquid mixtures, though the phenomenon occurs analogously in gases and perhaps even in solids. Similarly, the importance of the Dufour effect is given by the ratio D'/λ, which unfortunately can be measured in practice only for gases.[1]

For liquids, the thermal diffusion coefficient D' is principally accessible through its connection with the Soret effect.

In connection with the coefficient s_T we define similarly the thermal diffusion factor $\alpha = D'T/D$ and the thermal diffusion ratio $k_T = D'TN_1N_2/D$, where N_1 and N_2 are the mole fractions of the components in a binary mixture.

The above analysis seems to indicate that only the group of purely dissipative phenomena is suited to the experimental study of the Soret effect. In fact, it has long been known that certain hydromechanical processes can interact with thermal diffusion:

(i) in thermogravitation the velocity of convection is harnessed to intensify the separation,[2] and
(ii) in the Thomaes procedure[3] an accelerated separation is achieved by making use of a horizontal laminar flow.

Hitherto, study of co-operation between the velocity of the bulk movement and purely dissipative processes could only be treated in a simplified way. Now, however, application of the general evolution criterion established by Prigogine and Glansdorff[4] allows a much more precise and complete phenomenology.

When thermal diffusion is brought about, in a liquid, without any bulk movement, a "pure" or elementary Soret effect is obtained. Experimentally this procedure is of great importance as a reference for other methods.

We have applied this procedure to the study of aqueous solutions of some halides, and we present now some characteristic features of the results.

II. EXPERIMENTAL METHODS OF STUDY OF THE ELEMENTARY SORET EFFECT

A. Experimental Data

The general principle is to "protect" the separation (of components of a mixture) from the perturbing effects of convection by means of a positive temperature gradient dT/dz, in the same direction as the gravitational field.

The technique is simple and has been tested repeatedly:[5] the solution is placed between two perfectly horizontal plane surfaces, preferably of metal (good thermal conductivity), as rigid as possible, maintained at different temperatures (Fig. 1). These

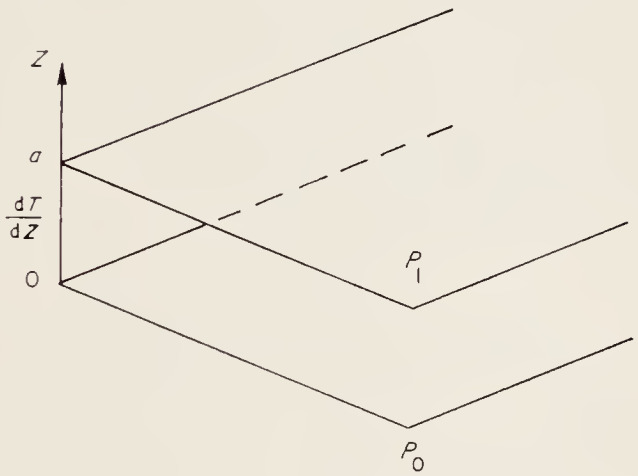


Fig. 1. P_0 and P_1 are parallel horizontal planes between which the solution lies; a is the thickness of the solution. The temperature increases vertically only, following the vertical coordinate axis $0z$.

details, seemingly trivial, are essential to the success of the experiments and will be discussed below.

In general we start with an isothermal solution and establish a temperature gradient within it. This first stage is very rapid by comparison with the time-constant θ of the diffusion process in a cell of appreciable depth (θ is of the order of 5,000–10,000 sec for a depth of 1 cm); its duration depends only on the thermal constants of the apparatus. It is usually assumed that the thermal diffusion process itself does not enter in this preliminary stage. The experimental reality is perhaps less clear-cut.

Whatever the macroscopic method of measurement used so far [refractive index gradient, or (for electrolytes) e.m.f. gradient or resistivity], the Soret effect is always manifested qualitatively, in a way strictly identical with the establishment of the temperature gradient, despite the fact that on the molecular scale the processes are, according to all the evidence, fundamentally different.

This experimental difficulty is additional to that resulting from the small amplitude observed in separations by the Soret effect ($s_T \simeq 10^{-3}$ deg^{-1}).

It follows that the whole art of the measuring procedure consists in choosing one or several parameters whose variations, sufficiently easily assessed, are an adequate guide to variations in concentration—the usual macroscopic expression of the Soret effect. To this end we choose, as function of concentration, a parameter insensitive to variations in temperature, such as the mass fraction, the mole fraction N, or (as here) the molality m of the dissolved component. The Soret coefficient of the binary mixtures studied will then be expressed as:

$$s_T = -\frac{1}{N_1 N_2} \cdot \frac{\mathrm{d}N_1}{\mathrm{d}T} = -\frac{\mathrm{d}\ln m}{\mathrm{d}T}. \tag{2}$$

Note. This formulation of the Soret coefficient results from that of Fick's general law, commonly used to describe thermal diffusion in such systems:

$$\boldsymbol{J}_1 = -DC(\boldsymbol{\nabla} N_1 + s_T N_1 N_2 \boldsymbol{\nabla} T), \tag{3}$$

where $\boldsymbol{J}_1$ is the flux of the dissolved substances, in moles per unit surface area per unit time, and C is the total number of moles per unit volume (molar density).

B. Thermodynamic Data

In the absence of chemical reactions and with the hypothesis that the velocity of convection cancels out, the entropy production of the systems now under consideration reduce to first-order tensor terms (as outlined in the Introduction) provided that we include a term representing the electrostatic field due to the ions. For the flux we can then write phenomenological expressions

(already given repeatedly) of the following type for each ionic species γ

$$\rho_\gamma \Delta_\gamma / M_\gamma = -L_{\gamma\gamma'}\{(\nabla\mu_{\gamma'})_{p,T} + z_{\gamma'}F\nabla\psi + (Q^*_{\gamma'}/T)\nabla T\} \qquad (4)$$

(summation over the index γ' implied, $\gamma' = 1, \ldots, c-1$)

where division by the ionic mass M_γ yields molar flux with respect to the reference velocity considered to be zero. The bracketed terms are "forces," *i.e.*, the different gradients existing in the electrolyte: gradients of temperature T, of electrostatic potential ψ or mean macroscopic field $\boldsymbol{E}$, and of chemical potential μ_γ of ion γ of valency z_γ, having molar heat of transfer Q^*_γ. This last quantity represents the amount of heat transported per mole of ion γ, diffusing when the system is isothermal and with no transport of enthalpy. This definition takes into account the Onsager reciprocity relations.

We consider as "ionic species" the solvate ion of each type, *i.e.*, ions surrounded by their permanent sheath of water molecules.

Taking into account the existence of relations such as the Gibbs–Duhem relations between chemical potential gradients and between quantities of transfer,† it can be shown that free solvent takes only a secondary part in eqns. (4).

Eqns. (4) lead readily to experimental quantities.

1. *The Soret coefficient*

This is obtained, as for Fick's law (3), by considering the steady state (often wrongly termed the Soret equilibrium), in which the fluxes vanish because the forces, taken separately, cancel out. Expressions are combined in order to eliminate $\nabla\psi$, and after simple rearrangement we have:

$$s_T = -\frac{\mathrm{d}\ln m}{\mathrm{d}T} = \frac{\nu_+ Q^*_+ + \nu_- Q^*_-}{m(\partial\mu/\partial m)T}, \qquad (5)$$

where ν_γ are the well-known stoichiometric coefficients, related to the ionic valencies by $\nu_+ z_+ + \nu_- z_- = 0$, and $\mu = \nu_+\mu_+ + \nu_-\mu_-$ is the chemical potental of the dissolved salt

† At constant temperature and pressure, we have:

$$N_\gamma \nabla\mu_\gamma = 0 \qquad \text{and} \qquad N_\gamma Q^*_\gamma = 0.$$

(summation over the index γ implied, $\gamma = 1, \ldots, c$)

2. *The electric potential gradient*

This gradient existing within the solution, may be expressed in terms of other gradients. One of the simplest methods is to assume that the macroscopic mean density of charge is zero, even during the diffusion process. We thus obtain an expression containing transport numbers t identical with those of Hittorf:

$$F\nabla\psi = -(t_\gamma/z_\gamma)(\nabla\mu_\gamma)_{p,T} - (t_\gamma/z_\gamma)(Q_\gamma^*/T)\nabla T. \tag{6}$$

(summation over the index γ is implied, $\gamma = 1, \ldots, c-1$)

When the Soret effect begins, the first term is zero. In the steady state, both terms participate in the expression for the potential, *i.e.*, we obtain two values for the potential gradient, in some way containing the phenomenon.

Under these conditions the experimental problem resolves itself into finding techniques capable of measuring, with the desired precision and reproducibility, the gradients of molality m, electric potential ψ, and temperature T. Further the requirement that the obstruction of the cell must be small (imposed by the conditions of development of the Soret effect) is taken into account.

C. Experimental Techniques

The following two techniques have been utilized.

1. The variations in concentration of the solution with time are followed by means of the resulting changes in refractive index with a Young–Rayleigh interferometric procedure.[6] Details have been given in a previous paper.[7] It is emphasized that the technique causes little perturbation if classical low-energy radiation is used.

The Soret coefficient is very simply calculated from the measurements by the relation

$$s_T = -\frac{1}{m}\cdot\frac{1}{(\partial n/\partial m)}\cdot\frac{\delta n/\delta z}{\delta T/\delta z} \tag{7}$$

(where n is the refractive index), which implies a knowledge of (i) the function $\partial n/\partial m(m)$ at the mean experimental temperature, a function which we have determined by appended goniometric

measurements, (ii) the temperature gradient $\delta T/\delta z$. To obtain this we made use[7] of the facts that, on the one hand, the refractive index of water at different temperatures and at a large number of wavelengths is very well known (to 7 decimal places) and that, on the other hand, the thermal conductivities of water and of aqueous solutions of halides at the same temperature are very similar, even when the concentration becomes important.

Under these conditions, a simple "thermal calibration" by interferometry with pure water yields the expected precision without any of the hazards associated with direct measurements.

2. A technique of potentiometric exploration by means of silver halide electrodes, placed directly in the interior of the diffusing medium, was effected[8]† in 1956 and has since been modified.[10] It requires electrodes which are 10–100 times more sensititive and reproducible than those in the usual electrochemical techniques. Readings have been taken by means of a high-quality balancing circuit.

Between the e.m.f.'s measured at the beginning of the effect and in the steady state there is a relationship depending explicitly on the Soret coefficient, which is readily obtained from eqn. (6) (cf. ref. 10):

$$\left(\frac{\delta\psi}{\delta T}\right)_\infty - \left(\frac{\delta\psi}{\delta T}\right)_0 = t^+ \cdot \frac{\nu}{\nu_+\nu_-} \cdot \frac{RT}{F}\left(1 + \frac{\partial \ln f^\pm}{\partial \ln m}\right) s_T, \qquad (8)$$

where the temperature coefficient due to the electrodes (a tricky problem) is eliminated (in the most general case, the ratio $\nu/\nu_+ z_+$ should be used instead of $\nu/\nu_+\nu_-$). In eqn. (8), $\nu = \nu_+ + \nu_-$, and $f^\pm$ is the mean ionic activity coefficient of the electrolyte.

D. Experimental Arrangement (Fig. 2)

The Soret cell A is traversed by monochromatic parallel light of which two beams are selected by the slits f_I and f_{II} The displacement of the interference fringes before the grating g in the reflex chamber R is received by the photomultiplier P and

† At about the same time Agar and Beck[9] made analogous measurements by using amalgam electrodes placed on both sides of the solution (thallium salts) contained in a Pyrex fritted disc.

registered by the light spot follower. Further, at the level of cell A the pair of measuring electrodes is shown, the active regions being horizontal.

E. Comments on the Methods Used

The use of two simultaneous techniques does not necessarily mean that both can be applied over the whole range of concentration studied ($m \simeq 10^{-3}$ to 3).

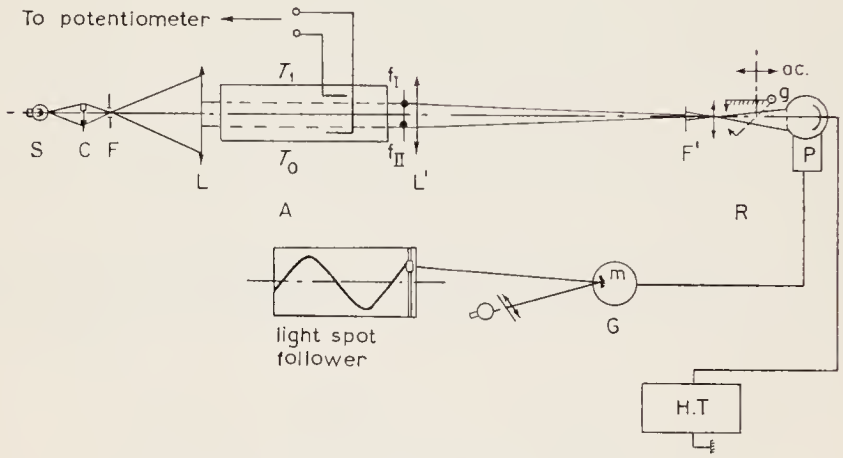


Fig. 2. Experimental arrangement.

In fact, the variation of refractive index, being approximately proportional to the absolute variation of concentration, decreases with it so that the interferometric method loses all effectiveness below $m = 0{\cdot}2$–$0{\cdot}5$ for the halides studied.

Potentiometric measurements, on the contrary, allow low concentrations to be investigated, until the increase in resistance of the solution makes the balancing-circuit method inaccurate. In concentrated solutions other limitations intervene. We note further that knowledge of the transport number to better than 2 per cent is superfluous, in view of experimental errors, when applying eqn. (8).

The two techniques are, then, mainly complementary. However, a comparative test is possible in the region where both apply.

III. THE ELEMENTARY SORET EFFECT IN CERTAIN AQUEOUS SOLUTIONS OF HALIDES

A. Phenomenological Considerations

If the real start of the Soret effect can be determined, the relative variation of concentration, or the variation of e.m.f. [related to it by eqn. (8)], takes a familiar exponential course. As a function of time, when the observation is made sufficiently far from the upper and the lower plane, a curve is obtained that is asymptotic to the horizontal straight line depicting the steady state (Fig. 3).

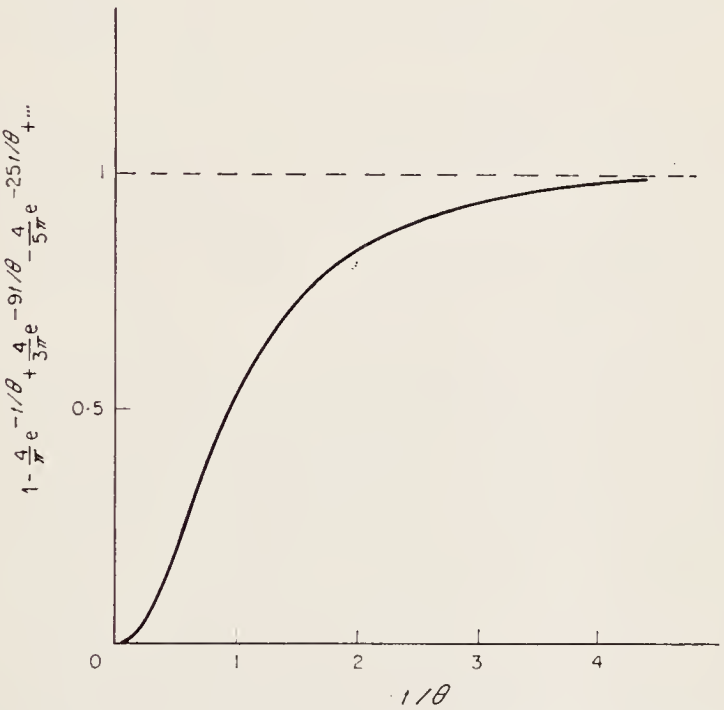


Fig. 3. Curve for the Soret effect at the half-depth of the cell ($z = a/2$), according to Bierlein's law. The dashed line indicates the stationary state.

The time constant θ of the process is, to a first approximation, related to the isothermal mutual diffusion coefficient D and the depth a of the cell (the distance between the metallic plane surfaces) by the eqn.

$$\theta = a^2/\pi^2 D, \tag{9}$$

which, for reasonable durations of observation of 400–500 min, allows only a small range of values around 1 cm for the height a. When D is known beforehand, application of eqn. (9) allows the value of experimental findings to be tested. On the other hand, θ has not so far been obtained with a precision that would allow D to be calculated to better than about 1·5 per cent.

Determination of the start. Using slits and electrodes symmetrical about the mid-plane of the cell, L. Mousselin seems to have verified, fairly successfully, Bierlein's phenomenological law[11] for the half-depth of the cell. This law takes the form of a series of exponentials:

$$1 - \frac{4}{\pi}\exp(-t/\theta) + \frac{4}{3\pi}\exp(-9t/\theta) - \frac{4}{5\pi}\exp(-25t/\theta) + \ldots$$

of which only the first is of interest for periods greater than $0{\cdot}5\theta$ (Fig. 3). Higher terms allow account to be taken of the initial part of the curve, which presents a tangential separation from the origin. Thomaes[6] was the first to establish the existence of this characteristic form.

A certain inaccuracy still exists in the placing of the instant $t = 0$. No doubt the Soret effect takes 20 or 25 times as long as the initial stage of establishing the temperature gradient if the steady state is sufficiently closely approached; but its progress, though much slower, is exponential, so that any error may be much more serious in the earliest moments. Experiments with the establishment of temperature gradient reduced to the minimum did not allow this question to be settled definitely.

Residual convection in the elementary-Soret-effect cell. In our experiments the reference level was nominally horizontal to about 4 seconds of arc. Whenever the cell was deliberately inclined a few minutes from the horizontal, the course of the curves altered considerably; the time constant bore no relation to the diffusion coefficient D, the value of the Soret coefficient was reduced to $\frac{1}{2}$ or $\frac{1}{3}$, etc.

The most obvious consequence of a deviation from the horizontal is the introduction of a horizontal component of the temperature gradient: a convection must thus arise which will constantly destroy a density stratification.

To what extent can it be assured that no residual convection exists in a normally regulated cell, despite all the precautions taken to avoid it? [The lateral walls of the cell are of glass, of thermal conductivity similar to that of water: $\kappa \simeq 0{\cdot}0018$ cal/(cm s deg).] Is the cell so nearly horizontal, and above all is the gradient so uniform over the whole surface, that the results

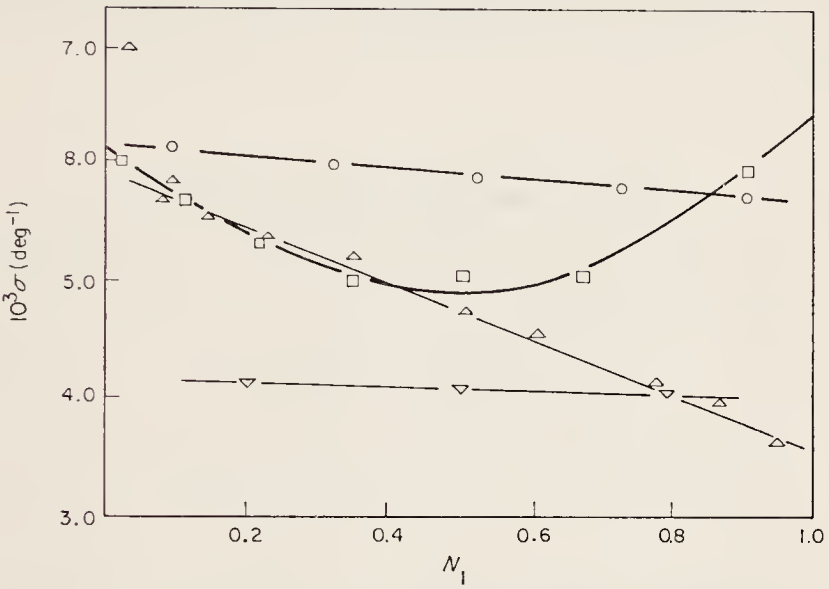


Fig. 4. Soret coefficient for CCl_4–cyclohexane. ○ Present work, flow cell, 25°C. □ Horne and Bearman, thermogravimetric column, 25°C. △ Thomaes, static cell, 26°C. ▽ Tichacek *et al.*, stirred diaph. cell, 40°C.

are free from systematic error, certainly by default, since the numerical values obtained show a certain scatter? Does the application of eqn. (9) constitute a sufficient guarantee?

It is timely to re-emphasize the discrepancies between experimental results from different methods of study of the Soret effect. We have encountered these disagreements several times for electrolytes in aqueous solution. They occur similarly with organic liquid mixtures,† where important discrepancies have been found (see Fig. 4).

† J. C. R. Turner, personal communication (Fig. 4).

Residual convection in the elementary Soret effect may not be the sole cause. It could well be that the phenomenological theories of thermogravitation in particular, as used so far, have been insufficiently developed (*e.g.*, the connection between thermal diffusion and velocity of the system).

What is this residual convection in the elementary Soret effect, and on what scale does it occur? Though it is improbable that it is a vast concerted movement of 10^{22} molecules, how can it be avoided? Classical experimentation is confronted by novel problems.

B. Results and General Considerations

We may eliminate the non-ideality factor $(1 + \partial \ln f^{\pm}/\partial \ln m)$ from the right-hand side of eqn. (5) and write, on the usual system:

$$s_T \left(1 + \frac{\partial \ln f^{\pm}}{\partial \ln m}\right) = \frac{\nu_+ Q_+^* + \nu_- Q_-^*}{RT^2} \tag{10}$$

$$= \frac{\nu_+ S_+^* + \nu_- S_-^*}{RT} \tag{10'}$$

where $S_\gamma^* = Q/T_\gamma^*$ is the entropy of transfer in Eastman's sense.

The general course of the experimental results is given by the curves of Figs. 5 and 6. For KCl, NaCl, $BaCl_2$, and $SrCl_2$ these graphs were constructed from a collection of results by Agar *et al.*,[12] Longsworth,[13] Snowdon and Turner,[14] Payton and Turner,[15] and the author.[8,16] For the other electrolytes, the determinations were made by Mousselin[10] who was the first to give the complete course of the variation of the quantities of transfer for a whole range of concentration, from one consistent series of determinations.

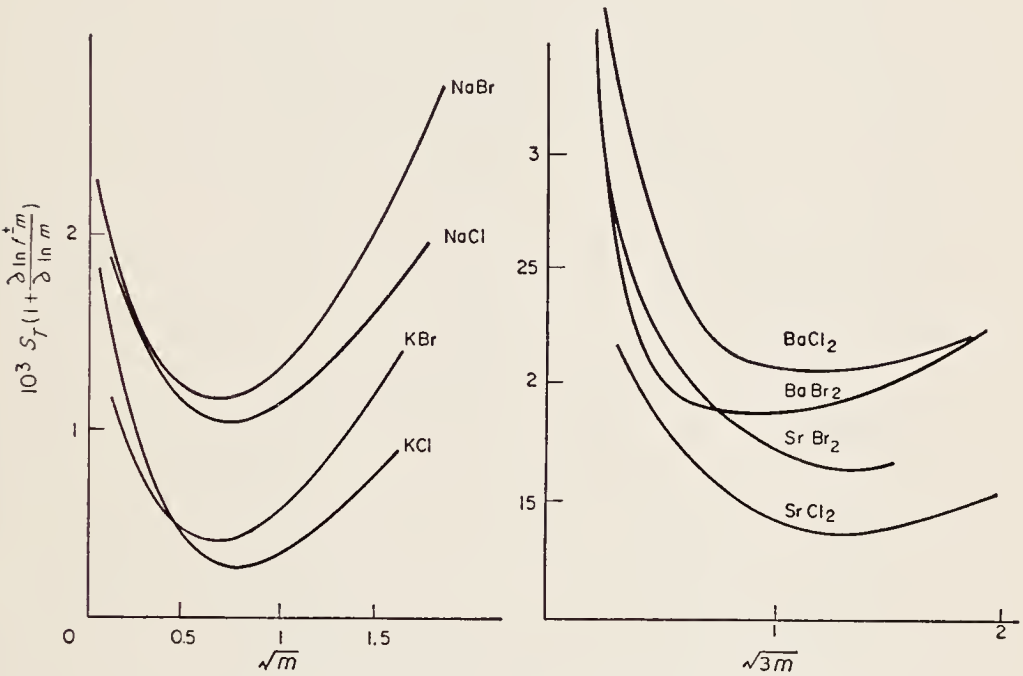
The graphs of Figs. 5 and 6 are interesting from two points of view.

First, the limiting values at zero concentration, for which Helfand and Kirkwood[17] and later Agar[12] established theoretical $\sqrt{m}$-laws. If the slopes actually obtained differ from that expected for 1:1 electrolytes for example, a similar $\sqrt{m}$-law seems to be

fully justified. Moreover, as suggested by Agar,[12] when the concentration remains low we may write:

$$\nu_+ S_+^* + \nu_- S_-^* = \Sigma_0^* + \nu R \left(\ln f^{\pm} + T \frac{\partial \ln f^{\pm}}{\partial T} \right). \qquad (11)$$

The experimental findings give a satisfactory constancy of Σ_0^* for alkali chlorides up to about alkali chlorides up to about 0·1m, but a less satisfactory constancy for the bromides (Figs. 7 and 8).

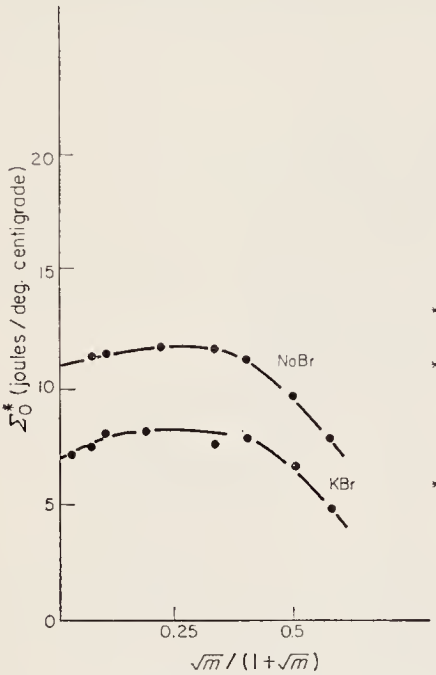


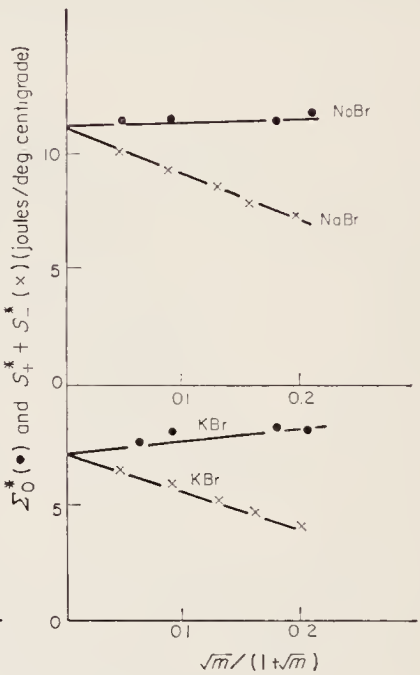
Figs. 5 (*left*) and 6 (*right*). Curves for chlorides and bromides.

Secondly, with regard to the general course of the variation with concentration, we note, for each of the eight electrolytes mentioned, the existence of a minimum, more pronounced with alkali metals than with alkaline earths; in fact, this minimum appears already in the behaviour of the Soret coefficient of the former, but not of the latter, at least up to concentrations of $m = 1{\cdot}5$ which were investigated. We note similarly the surprising position of the $BaBr_2$ curve, which over a wide range lies below that of the chloride.

To what extent can the minimum, thus observed, be considered sufficiently indicative of the behaviour, with varying concentration, of transfer quantities of aqueous ionic media?

The following considerations, based on very restricted results, should not be taken as a justified explanation of the real situation, but rather as an indication of lines of research. It is re-emphasized





Figs. 7 (*left*) and 8 (*right*). Limiting values.

that, among the electrolytes studied, only the alkali-metal group seems sufficiently consistent (Fig. 5), and that the molality at the minimum can be very approximately fixed at $m = 0{\cdot}40$ for the two bromides and $m = 0{\cdot}53$ for the two chlorides.

Though apparently remote from our present problem, experiments confirming Enskog's theory of hard spheres show that in a pure gas the variation with density, of certain transport processes (viscosity, heat conduction) has a minimum. Fig. 9 reproduces curves, from Iwasaki and Kestin,[18] of viscosity of a mixture showing an extremum, characterized as a function of composition.

In this framework it would be more interesting to see what is disclosed by the parameters of thermal diffusion, but in general the expressions are not analytically simple (Rice and Alnatt[19]). Such an approach would certainly be very dangerous unless we made only the limited statement that the behaviour revealed for the electrolytes studied in aqueous solution (as to the progress of thermal diffusion as a function of composition) is rather trivial.

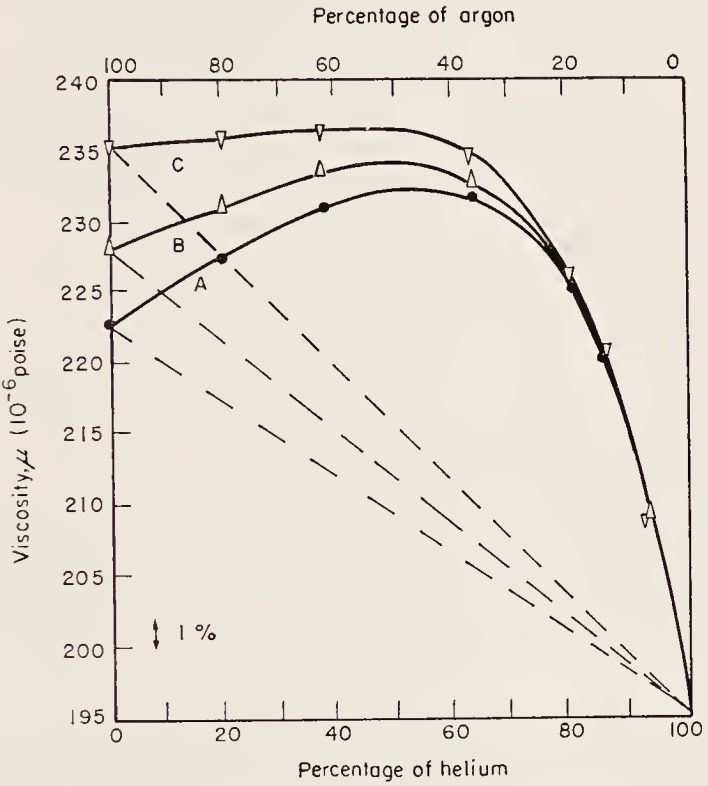


Fig. 9. Viscosity of argon–helium mixtures at 20°C and (*A*) 1, (*B*) 25, and (*C*) 50 atm. [Reproduced, by permission, from H. Iwasaki and J. Kestin, *Physica*, **29**, 1345 (1963).]

What, then, can be said concerning, more particularly, electrolytes in aqueous solution?

(i) In the first place, if eqn. (11) is made to play a part other than that of the limiting law at zero concentration, we can predict, qualitatively, the existence of a minimum for $S_+^* + S_-^*$ as a

function of m, but at a position somewhat removed from that found by experiment.†

We note that the theory is based essentially on considerations of ionic interaction, the intervention of the solvent being manifested only through the coefficients $f^{\pm}$ and $\partial f^{\pm}/\partial T$.

(ii) Without discussing thoroughly the various possible models, we can, from the hypothesis by Frank and Wen[20] after Gurney,[21] present on phenomenological bases (deliberately much simplified) certain points of view which appear to be, on the whole, not inconsistent with the shape of the experimental graphs.

The principal idea consists in insisting on the localized character of the heat of transfer Q_γ^* without neglecting long-range interactions. Following Tyrrell,[22] we may say that it represents the amount of heat that must be supplied to, or withdrawn from, the surroundings of an ion in order to maintain the temperature constant when this ion changes its position, the heat quantity being freed from the exchanged enthalpy.‡

According to Frank and Wen, three of the four univalent ions§ exist in dilute solution in conformity with the model in Fig. 10. Around the central ion, there are: a first layer A of water molecules strongly bound by powerful interactions of the "charge-moment–induced-moment" type; a second layer B where the ionic field is still strong enough to suppress the "normal" water structure (the structure-breaking region, less "ordered" than pure water); a third region C where a certain dielectric polarization of "structurally normal" water would also be expected.

This last long-range interaction would make a positive contribution to Q_γ^* at high dilutions; this contribution would decrease rapidly with rise in concentration on account of a mutual "screening" effect of the ions.[21] In this first stage the structure-breaking zone would be little altered, so that its contribution to Q_γ^*, which is negative (cf. layer B, above), would remain constant. As soon as the number of ions is high enough for zones B to touch, or even to encroach on each other, there would be a decrease in the negative contribution to Q_γ^*, *i.e.*, a relative increase in this transfer

† H. J. V. Tyrrell, personal communication (ref. 22).

‡ The sign of Q_γ^* depends on the direction of the heat exchange.

§ Na^+ probably would not show a strict "breaking" structure.

quantity. Hence arises a possible minimum, to be superimposed on that due to purely ionic intreactions. But this elementary explanation must not make us overlook the enormous complexity of the problem as met in reality.

If we look for the order of magnitude of the number of water molecules bound in the structure-breaking region by a univalent ion, near the minimum, and if we assume equal numbers for the

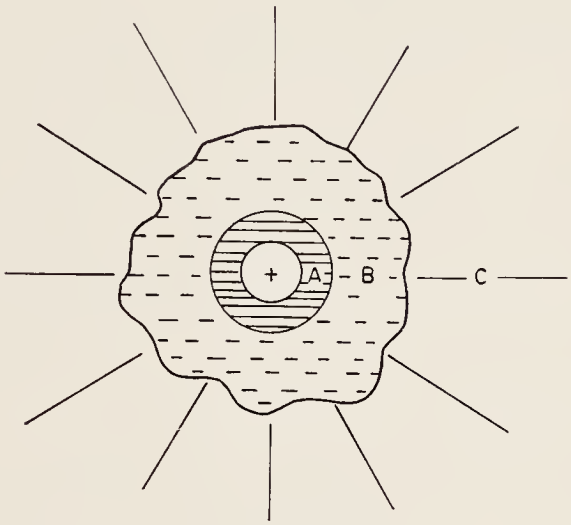


Fig. 10. Simple model for the modification of the structure of water by a small ion. For the meaning of *A*, *B*, *C* see text. [Reproduced, by permission, from H. S. Frank and W. Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).]

cation and the anion, we find 50–68 for K^+ and Na^+, 50 for Cl^-, and 68 for Br^-. These numbers are close to the maximum for a second concentric layer of water molecules, assumed spherical, around a central ion of the same size (*e.g.*, K^+ ion), *i.e.*, 63.

Similarly we may calculate the differences in entropy of transfer for the common cation, then for the common anion, in the region of the minimum; we find (joule $mole^{-1}$ deg^{-1}):

$$S^*_{NaBr} - S^*_{NaCl} = 0{\cdot}74$$
$$S^*_{KBr} - S^*_{KCl} = 0{\cdot}62$$
$$S^*_{NaCl} - S^*_{KCl} = 3{\cdot}60$$
$$S^*_{NaBr} - S^*_{KBr} = 3{\cdot}72$$

When we consider that the ionic contributions are not independent, the system appears very consistent.

Non-aqueous polar solvents. It is of interest to see how thermal diffusion occurs in electrolytes dissolved in polar solvents other than water. Very recently, Bierlein† has achieved measurements in solvents of different dielectric constant ε. Fig. 11 and 12 reproduce his results for KBr and KI in formamide ($\varepsilon = 109$) and dimethylformamide ($\varepsilon = 36$).

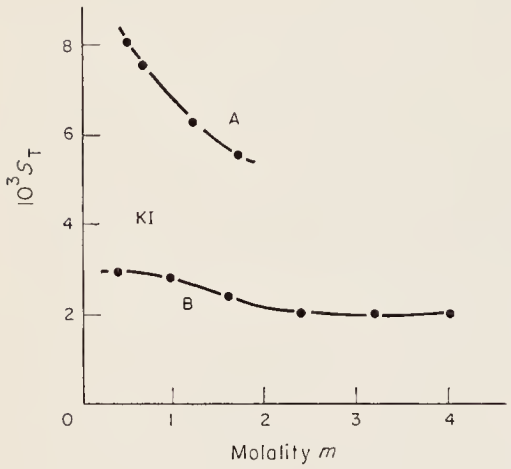


Fig. 11. Soret effect for KI in (*A*) dimethylformamide and (*B*) formamide.

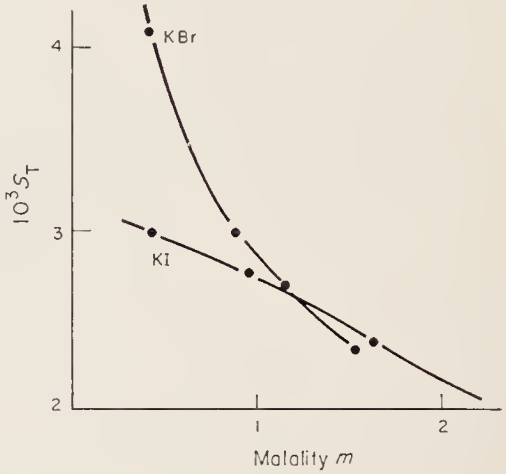


Fig. 12. Soret effect for KBr and KI in formamide.

It is pointed out that Frank classifies the I^- ion in the same group of "structure-breaking" ions as the majority of those listed here, but, without knowledge of the non-ideality factor $(1 + \partial \ln f^{\pm}/\partial \ln m)$, it is difficult to be conclusive. It is noted, however, that monotonic variations would seem to be the rule in this type of solution.

IV. CONCLUSIONS

Although the number of experimental instances remains insufficient for valid conclusions to be drawn, it seems desirable, in spite of considerable difficulties (notably theoretical), to attach

† C.I.T.C.E., Budapest 1965.

more importance than hitherto to the role of the solvent when studying thermal diffusion in aqueous ionic media. But, before this, ought we not to try to free the experimental findings, coming from various methods, from that measure of uncertainty which, too often, still restricts the extent of direct comparison?

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